Precise Measurement of the PVT of Polypropylene and Polycarbonate up to 330°C and 200 MPa

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ABSTRACT: An apparatus for measuring the pressure–volume–temperature (PVT) properties of polymers using a metal bellows has been developed at temperatures from 313 to 623 K and pressures up to 200 MPa. A calibration of the device was performed by measuring PVT of mercury and water. The experimental uncertainty of specific volumes was estimated to be within ±0.2%, while that of temperatures was within ±0.1 K below 300°C and ±0.3 K above 300°C. The estimated uncertainty of pressures was ±0.1 MPa below 100 MPa and ±0.25 MPa above 100 MPa. The PVT properties of polypropylene and polycarbonate were measured by the apparatus in the temperature ranges from 40 to 300°C and from 40 to 330°C, respectively, and pressures from 10 to 200 MPa. The effects of a sample cup and sample forms were investigated. The use of the sample cup showed a little effect on the measurments of PVT properties for both samples. The shape (pellet and pillar) of the samples caused a small difference in the specific volumes only under high temperatures and low pressures. The PVT properties in a melt state were correlated by the Simha-Somcynsky equation of state, showing a good agreement with measurements. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 141–150, 1997

Key words: PVT; polypropylene; polycarbonate; Simha-Somcynsky EOS

INTRODUCTION

It is important to grasp properties of polymer systems from the standpoints of the optimal design, the process control, and the savings of energy and resources in polymer industries. Authors[1–3] have investigated solubilities of organic solvent vapors and high-pressure gases in polymers, which are important for the analysis of devolatilization processes and foaming processes. In these works, the PVT (Pressure–Volume–Temperature) properties of polymers are necessary to correlate and predict the solubilities using equations of state.

On the other hand, simulations of an injection-molding process of polymers have been developed in recent years. The simulations require many properties of polymers such as the PVT, thermal conductivity, viscosity, and heat capacity over wide ranges of temperatures and pressures. The PVT is considered to be one of important properties to predict final shape and size of molded polymers. Although the PVT properties of polymers have been investigated by several authors, the data for the same polymer are not in agreement with each other, because of the difference in apparatuses, methods, and samples used in the experiments.

The techniques for the PVT measurement of polymers are classified into two principal methods[4]: a piston method, and a confining-fluid method. In the former, a polymer sample is introduced in a cylinder and a pressure is applied to it by a piston.[5] The volume change of the polymer

is determined from the motion of the piston. While the method is simple, a leakage of the polymer may occur through a gap between the piston and the cylinder if the polymer is in a melt state, and the pressure is not hydrostatic[6] if the polymer solidifies by crystallization or glass formation. For these reasons, the piston method may not be adequate for accurate measurements. In the latter method, a polymer sample is immersed in an inert confining fluid such as mercury to surround the sample in a dilatometer. The role of the confining fluid is to provide a hydrostatic pressure even for a solid sample. The total volume change of the sample and the confining fluid is measured in diverse manners.[7,8] To determine the volume change of the sample itself, corrections for the known PVT properties of the confining fluid are needed. The confining-fluid method may be suitable to accurate measurements because the leakage of the sample and the nonhydrostatic pressure can be prevented.

An apparatus reported by Zoller et al.[8] is well known as a typical example of the confining-fluid method. A dilatometer composed of a flexible metal bellows was filled with a polymer sample and mercury as a confining fluid. The dilatometer was sealed, pressurized, and heated in a pressure vessel. The total volume change in the dilatometer was determined by the motion of the bellows and its effective cross-sectional area. They determined the PVT of polymers from the difference in the motion of bellows obtained two experimental runs at the same temperature and pressure; namely, a run using a polymer sample with mercury and a blank run using only mercury, to cancel out the effect of the expansion or compression of materials used as the dilatometer. Therefore, they cannot get the PVT of mercury. Moreover, corrections for the volume change of mercury were carried out using an empirical equation. This equation fitted using literature[9] values up to 191°C, however, showed systematic deviations from the work of Beattie et al.,[10] whose data at an atmospheric pressure were believed to be accurate and reliable (this will be described afterward). The specific volume calculated by the equation deviated −0.17% from Beattie's data at atmosphere and 350°C. In this work, a different calibration method that can get the density of mercury was adopted.

In the previous work[11] we constructed an apparatus suitable for the accurate PVT measurements of polymers over a temperature range from 40 to 200°C and pressures up to 200 MPa based on the bellows method. The present work has modified the apparatus to elevate the maximum temperature up to 350°C. To do this, the influence of temperature, pressure, and the length of the bellows on the inner volume of the dilatometer was investigated in detail, comparing measured PVT properties of mercury and water with reliable literature values. PVT properties for polypropylene and polycarbonate were measured using the apparatus.

Although the confining-fluid method is advantageous for the hydrostatic pressure, a similar situation to a piston method may also occur,[12,13] when a sample solidifies and adheres to dilatometer walls during a cooling process. To avoid this, a technique has been proposed[13,14] where the polymer sample was wrapped with a cap (a sample cup called by He et al.[13]) formed of thin Teflon or nickel foil. He et al. found a marvelous effect of the sample cup on the improvement in PVT measurements performing isobaric cooling and isothermal compression experiments. In the present work, we carried out isothermal compression experiments changing temperatures from lower to higher temperatures (opposite direction to those by He et al.) starting with a solid sample. The solidification and adhesion may occur only in a narrower range when the polymer melted by heating is compressed beyond its glass transition point or melting point. The effect of the sample cup in this isothermal experiment has been investigated in the present work.

The present work has also investigated the initial forms of samples put into the dilatometer. It is convenient to use pellet samples as received, because the molding of samples may cause changes in the crystallinity and the molecular weight distribution. To measure PVT properties accurately, however, a large amount of samples should be put into the dilatometer. Molding of samples enlarges the bulk density and reduces surface area. Furthermore, a large surface tension of mercury may have influence on measured data using samples of different surface areas.

EXPERIMENTAL

Dilatometer

Figure 1 shows a cross-sectional view of the dilatometer used in this work. The dilatometer consists of a sample-filling section and a bellows. The total inner volume is about 9.3 cm³ in a relaxed
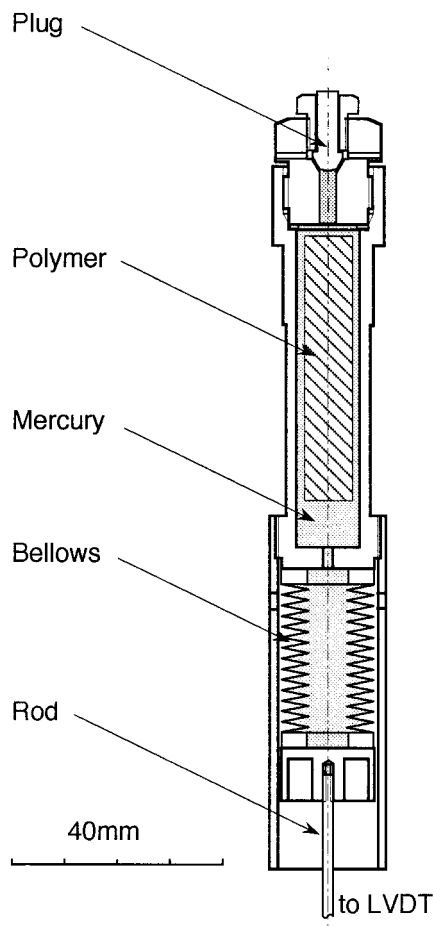
Figure 1   Dilatometer.

condition. The sample-filling section is made of 316 stainless steel, and its inner volume is about 6.8 cm³. The welded type bellows (Nippon Valqua Industries Ltd.), which is made of stainless steel (AM350), is used because of its character of low hysteresis and low spring constant. The inner and outer diameters of the bellows are 8 and 18 mm, respectively, and the length is allowed to vary from −8 to +12 mm against the relaxed condition. The top of the sample-filling section is sealed by iron gasket and corn plug, while the bottom is welded at one end of the bellows. A nonmagnetic stainless steel rod with an iron core in the bottom is connected at another end of the bellows to determine the displacement of the bellows by using a linear variable differential transformer (LVDT).

The maximum amount of sample placed in the dilatometer is about 5 cm³. In this work, the volume ratio of the polymer sample to mercury is ranging from 0.5 to 1.1, which is much higher than 0.2 in the case of Zoller et al.[8] The higher

volume ratio of polymer should reduce the experimental errors in the polymer volumes.

Apparatus

Figure 2 illustrates a schematic view of the experimental apparatus. It mainly consists of five sections: a pressure vessel, temperature controllers, a hand pump, pressure gauges, and a section for the displacement measurement. The dilatometer is inserted in the pressure vessel, which is made of Inconel, a high-strength alloy. Brass cast heaters divided into five parts are surrounded the pressure vessel. Temperatures of the heaters are independently controlled by PID controllers. The temperature of a pressure-transmitting fluid (silicone oil) is measured with a high-pressure thermocouple (Butech Pressure Systems, type-K), which is horizontally inserted in side wall of the pressure vessel. Because of a large heat capacity of the
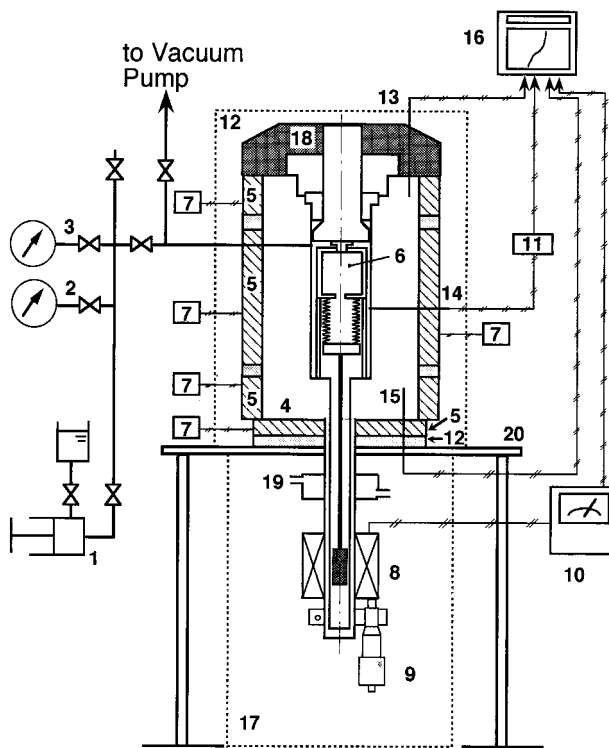

Figure 2   Schematic diagram of the PVT apparatus: (1) hand-operated pump; (2) pressure gauge (0–250 MPa); (3) pressure gauge (0–100 MPa); (4) high-pressure vessel; (5) cast heater; (6) sample cell; (7) PID controller; (8) LVDT; (9) micrometer; (10) displacement meter; (11) digital multimeter; (12) heat insulator; (13–15) thermocouples; (16) recorder; (17) thermostated air bath; (18) aluminum cover; (19) cooling jacket; (20) stand.

pressure vessel and the isothermal manner of the PVT experiments, the temperature measured in this work gives very small fluctuation (± 0.03 K) and difference from that of the sample in the dilatometer. The thermocouple as well as a digital multimeter had been calibrated against an intelligent RTD probe (Kays instruments inc., model X0860, accuracy $\pm$ 0.01 K). The accuracy of the temperature measurement is estimated to be within ± 0.1 K at temperatures up to 300°C and ± 0.3 K above it. The dilatometer is pressurized by the silicone oil in the pressure vessel using the hand pump. The pressure is read on one of two precision Heise gauges (Dresser Industries, model CM, F.S. 100 and 250 MPa), which had been calibrated against a dead weight tester (Pressurements Ltd., model M2800). The accuracies of these gauges are equally 0.1% of their full scales. The pressure difference between inside and outside of the dilatometer based on the elasticity of the bellows is estimated to be less than 18 kPa, which is negligibly smaller than the accuracy of the pressure measurement by the Heise gauges. The displacement of the bellows is determined by a micrometer (Mitsutoyo co. Ltd.) as well as the LVDT (Shinko Electric co., Ltd.) as a null detector with an accuracy of ± 2 μm. The section for the displacement measurement is thermostated at 308 K.

Calibrations

In the bellows method it is necessary to examine the relationship between the inner volume of the dilatometer and the displacement of the bellows. The present work determined a calibration equation for this purpose by comparing measured PVT properties of mercury[15] and water[16] at various conditions of temperatures and pressures with literature values.

When pressure was applied to the dilatometer confining solely mercury in it, a sudden decrease in effective cross-sectional area of the bellows was observed at low pressures less than about 5 MPa. This phenomenon was not observed in case of water as the confining fluid. The reason may be that mercury could not be stuffed into gaps of the bellows at low pressures, because mercury has high interfacial tension and low wettability. For this reason, PVT measurements were not carried out at pressures less than 10 MPa. The specific volumes of mercury at atmosphere were calculated by extrapolation of isothermal data in pressure

range from 10 to 200 MPa using the Tait equation.[17]

Inner volume measurements of the dilatometer were carried out three times. To vary the displacement over a wide range, two mixtures of mercury and water (volume ratios of mercury and water were 1 : 1 and 4 : 1) and pure mercury were used in these measurements. From the results the calibration equation was determined as follows:

$$V = [V_0 + A_0(1 + \gamma \Delta X)\Delta X]$$
$$\times (1 + \alpha \Delta T + \beta \Delta P) \quad (1)$$

where V_0 and A_0 are the inner volume of the dilatometer and an effective cross-sectional area of the bellows at a standard state, which is set at 313.2 K and 10 MPa for the reason described above. ΔX, ΔT, and ΔP are the displacement of the bellows, the differences in temperature, and pressure from the standard state, respectively. Parameters α and β are correction factors of the inner volume due to the temperature and pressure changes, respectively. In this work, it has become apparent that the effective cross-sectional area of the welded-type bellows depends on the displacement. Then correction factor γ for the effective cross-sectional area change was introduced in the equation.

The four parameters of A_0, α, β, and γ were determined from three isotherm experiments at 313, 373, and 423 K by a nonlinear least-squares method. The values of A_0, α, and β approximately agreed with values estimated from material properties and size of the dilatometer. The change in the effective cross-sectional area (about 1.3 cm^2) with the displacement was less than 4.7% in the range of the displacement from -5 up to $+7$ mm. The deviations of the inner volume calculated by eq. (1) from literature volume data were shown in Figure 3. The average and maximal deviations were 0.02 and 0.04%, respectively.

The parameters in eq. (1) were determined in relatively narrow range of temperature (313–423 K) and the displacement ($-3-+4$ mm). The PVT measurements of polymers will be carried out in wider ranges than these. Therefore, in order to confirm the applicability of eq. (1), PVT measurements of pure mercury and pure water were carried out. The ranges of temperatures, pressures and the displacements at the PVT measurements of water were 313–473 K, 10–200 MPa, and $-5-$ $+7$ mm, respectively. The measured specific volumes of water agreed with literature[16] values
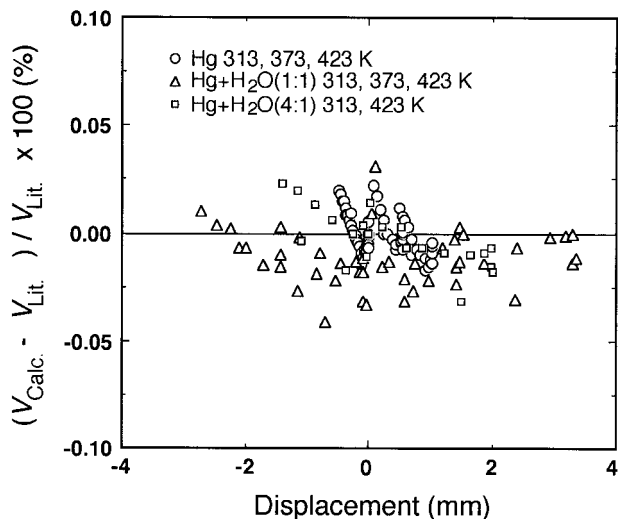
Figure 3 Comparison between experimental and literature volume data.

within ±0.05%, and the average deviation was 0.03%. The PVT of mercury was measured in the range of temperatures 313–623 K and pressures 10–200 MPa. The specific volumes of mercury at atmosphere determined using extrapolations of high pressure data under each isotherm were in good agreement with compilation values by Bigg[18] and experimental values of Beattie et al.[10] within 0.01% over the experimental temperatures. The experimental values of mercury determined in this work were used to get the PVT properties of polymers.

The changes in specific volume of polymers, Δv_P are determined using eq. (2)

$$\Delta v_P = [V - V_0 - (v_{Hg} - v_{Hg0})m_{Hg}]/m_P \quad (2)$$

where v_{Hg} is the specific volume of mercury, and subscript 0 denotes the standard state described above, and m_{Hg} and m_P are masses of mercury and polymer, respectively. The uncertainty in the specific volume measurements was estimated to be ±0.2% based on error analysis.

Procedure

The dilatometer is filled with mercury under vacuum after the polymer is placed in it. To keep constant volume of the dilatometer at the filling, the dilatometer is closed under restraining the bellows to a fixed position. The mass of the polymer and mercury in the dilatometer is weighed with an uncertainty of 0.2 and 2 mg, respectively.

The dilatometer is tightly fixed subsequently in the high pressure vessel with a spring. Procedures of PVT measurements for polymer are in the following manner. Pressure is applied for phasing into a desired value from low to high pressure under an isotherm and then the displacement measurements are carried out after confirmation of its constant readout. A time required to get one experimental point at a fixed temperature and pressure is generally about from 3 to 10 min, except for the transition region. This procedure is repeated from minimal up to desired maximal temperatures.

Sample

Polypropylene as a crystalline polymer and polycarbonate as an amorphous polymer were used in PVT measurements. The polypropylene (isotactic fraction 97%, $\bar{M}_w = 2.1 \times 10^5$, $\bar{M}_n = 5.2 \times 10^4$) was supplied from Idemitsu Petrochemical Co., Ltd. The polycarbonate ($\bar{M}_w = 6 \times 10^4$) was obtained from Scientific Polymer Product.

Two kinds of sample forms, pellets and pillar, were used in this work. Each polymer was molded into a pillar (about ϕ 11 mm) by a compression-molding machine consisting of a piston and a cylinder. The moldings were carried out in the following manner. The polymer was put into a cylinder of the molding machine, and was heated up to about 30 K higher than its melting point temperature under vacuum. When the polymer became a melt state, a pressure was applied by the piston. The both pillar polymers, polypropylene and polycarbonate, were annealed at 433 and 423 K, respectively, in a vacuum oven for 12 h. The densities of the pillar samples were measured by a hydrostatic weighing method. That of polycarbonate pellets (ϕ 2 × 2 mm) was measured by a sink-float method. The samples used in the PVT measurements were dried in vacuum after density measurements and their masses were from 3.2 to 4.2 g.

RESULTS AND DISCUSSION

Reproducibility

To confirm reproducibility of the PVT measurement, two polypropylene samples molded in the same condition were tested. The measurements were carried out for pillar samples without a sample cup. Their density, 1.1091 ± 0.0002 cm^3/g
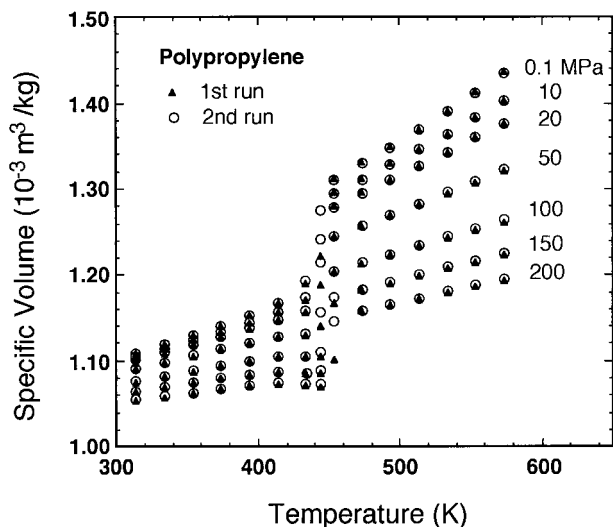
Figure 4 Experimental PVT results for polypropylene.

be evidence of increasing in crystallinity by pressurization. The two experimental results showed a good agreement with each other within ±0.1%, except for the transition region, as shown in Figure 4. It was too difficult to determine specific volume of first run at 443.8 K and atmosphere by extrapolation, because the isothermal data were scattered in this transition region.

The experimental results were compared with those of Zoller[19] in the melt state, where the sample was in a thermodynamic equilibrium. The comparison was good within ±0.25% above 50 MPa, while a systematic deviation from Zoller's data (max. +1.1% at 573.6 K and 0.1 MPa) was observed at high temperatures and low pressures. Our results, however, were in excellently good agreement (average absolute deviation 0.15%) with the experimental results presented recently by He and Zoller.[20]

Effect of Sample Cup

To investigate the effect of the sample cup in isothermal measurements, the PVT properties for polypropylene and polycarbonate were measured using samples wrapped with stainless steel foil (10 μm thick).

The experimental results of polypropylene are shown in Figure 5, except for the data at 443.8 K and atmosphere, because of the same reason

(40°C, 1 atm) agreed well with each other. The experimental results of PVT properties of the samples are shown in Figure 4 and the values of second run are tabulated in Table I. A melting point temperature of the polypropylene at atmosphere is observed about 440 K. The polypropylene is in melt state above the melting point temperature, and in rubbery state below it. The specific volume data at 433.8 and 443.8 K under high pressures were lower than that of 414.0 K. It may

Table I Experimental Specific Volume (10^{-3} m³/kg) Results for Polypropylene

Temp. (K)	Pressure (MPa)						
	0.1	10	20	50	100	150	200
313.0	1.1091[a]	1.1049	1.1009	1.0905	1.0764	1.0647	1.0546
333.4	1.1189[b]	1.1142	1.1096	1.0982	1.0822	1.0694	1.0583
353.6	1.1295[b]	1.1241	1.1189	1.1058	1.0884	1.0745	1.0628
373.8	1.1401[b]	1.1339	1.1280	1.1135	1.0945	1.0795	1.0671
393.9	1.1521[b]	1.1448	1.1379	1.1213	1.1004	1.0843	1.0711
414.0	1.1665[b]	1.1569	1.1480	1.1284	1.1050	1.0878	1.0739
433.8	1.1939[b]	1.1740	1.1577	1.1310	1.1045	1.0863	1.0722
443.8	1.2744[b]	1.2417	1.2150	1.1564	1.1105	1.0881	1.0727
453.6	1.3099[b]	1.2940	1.2793	1.2445	1.2038	1.1735	1.1464
473.5	1.3294[b]	1.3111	1.2948	1.2576	1.2141	1.1826	1.1576
493.5	1.3487[b]	1.3283	1.3104	1.2701	1.2243	1.1913	1.1654
513.4	1.3691[b]	1.3461	1.3263	1.2829	1.2343	1.2001	1.1731
533.6	1.3898[b]	1.3643	1.3428	1.2956	1.2446	1.2088	1.1807
553.7	1.4119[b]	1.3832	1.3593	1.3088	1.2544	1.2175	1.1884
573.6	1.4348[b]	1.4026	1.3765	1.3221	1.2648	1.2259	1.1959

[a] Hydrostatic weighing method.
[b] Extrapolated.
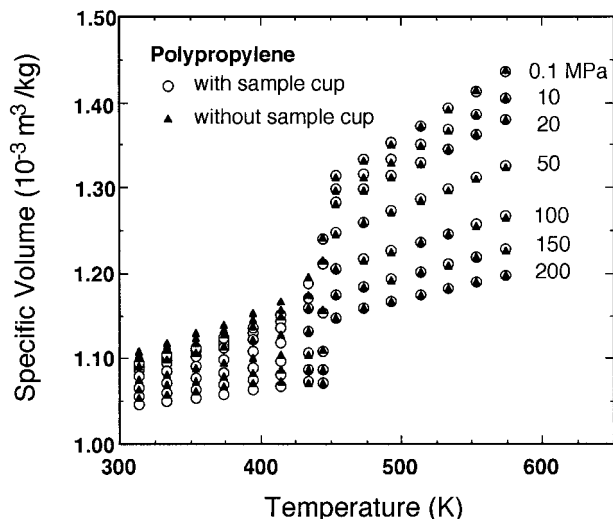
Figure 5 Experimental results of PVT for polypropylene with and without a sample cup.

Figure 7 Experimental results for polycarbonate of the pellet and the pillar.

mentioned above. A small difference can be observed in the specific volumes of polypropylene measured with and without the sample cup below melting point temperature, because crystallinities of both samples were different, i.e., 76.7 and 66.1 wt % determined by a density at 25°C and atmosphere, respectively. The specific volumes of two experiments were not in accordance with each other below the melting point temperature, although they have similar temperature and pressure dependences. However, the two experimental results above the melting point temperature agreed within 0.15%.
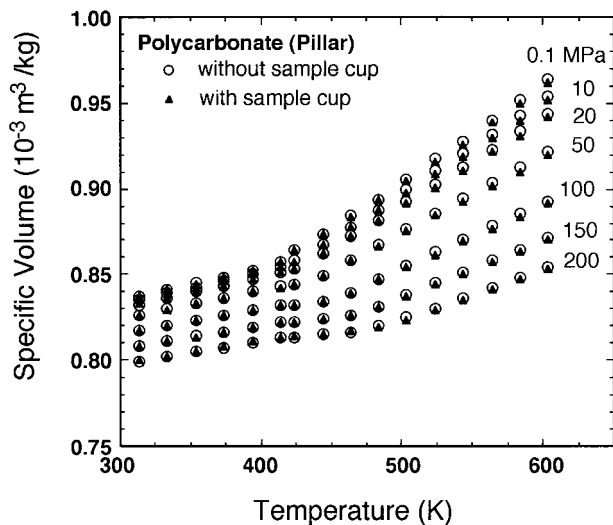

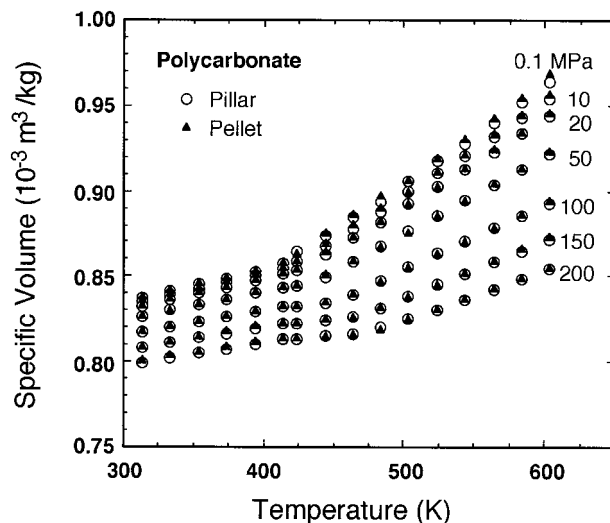**Figure 6** Experimental results of PVT for polycarbonate with and without a sample cup.

The experimental results of polycarbonate are shown in Figure 6. A glass transition temperature of the polycarbonate at atmosphere is observed about 415 K. The two experiments agreed within 0.2%, and an average absolute deviation is 0.04%. The solidification and adhesion may occur in the narrow range of the glass transition; the agreement, however, was especially good in glass and glass transition region.

As mentioned above, a clear effect of the sample cup was not shown in the isothermal measurements in this work.

Effect of Sample Forms

To investigate an effect of sample forms on the measured specific volumes, experiments carried out for polycarbonate of pillar and pellet forms. No bubbles in the pellet samples were confirmed by observation and density measurements. The density of pellets was 0.1% lower than that of the pillar at 40°C and atmospheric pressure. The reason of density difference may be due to their thermal histories. The PVT results of polycarbonate in pillar (ca. o.d. ϕ 11 × 40 mm, 4.2 g) and pellet forms (ca. ϕ 2 × 2 mm, 3.2 g) are compared in Figure 7. Open circles and triangles denote the measured results for pillar and pellet samples, respectively. Specific volumes of the pillar sample were a little lower than that of pellet at 463 and 483 K and below 10 MPa. It seems that a very small amount of crystalline is formed during the measurements in the pillar sample as described

Table II   Experimental Specific Volume (10^{-3} m³/kg) Results for Polycarbonate

Temp. (K)	Pressure (MPa)						
	0.1	10	20	50	100	150	200
313.2	0.8376[a]	0.8353	0.8328	0.8266	0.8168	0.8079	0.7995
333.6	0.8413[b]	0.8389	0.8365	0.8300	0.8198	0.8108	0.8023
353.7	0.8449[b]	0.8425	0.8399	0.8333	0.8230	0.8138	0.8049
373.8	0.8488[b]	0.8463	0.8436	0.8367	0.8262	0.8167	0.8077
393.9	0.8527[b]	0.8501	0.8473	0.8401	0.8294	0.8196	0.8105
414.0	0.8573[b]	0.8544	0.8511	0.8434	0.8321	0.8222	0.8130
423.8	0.8640[b]	0.8580	0.8535	0.8444	0.8326	0.8227	0.8135
443.7	0.8738[b]	0.8678	0.8627	0.8497	0.8346	0.8241	0.8148
463.6	0.8841[b]	0.8777	0.8721	0.8583	0.8393	0.8261	0.8164
483.5	0.8934[b]	0.8872	0.8817	0.8670	0.8469	0.8312	0.8198
503.3	0.9061[b]	0.8994	0.8930	0.8770	0.8556	0.8387	0.8249
523.6	0.9175[b]	0.9102	0.9030	0.8859	0.8630	0.8453	0.8306
543.5	0.9281[b]	0.9203	0.9130	0.8946	0.8705	0.8518	0.8365
563.6	0.9402[b]	0.9315	0.9231	0.9034	0.8781	0.8584	0.8424
583.5	0.9517[b]	0.9423	0.9334	0.9123	0.8854	0.8649	0.8483
603.4	0.9643[b]	0.9538	0.9439	0.9213	0.8928	0.8716	0.8542

[a] Hydrostatic weighing method.
[b] Extrapolated.

by Zoller.[21] The pelltes sample, however, did not observe the crystalline forming, and the sample used in this work did not show the melting point peak in a DSC measurement.

The PVT data of both the samples almost agreed within 0.2% over the whole range of the experiments, except for the crystalline-forming region. The experimental specific volumes of the pellets, however, showed systematically a little higher value than that of the pillar under the low-pressure and high-temperature region. The measurements may, consequently, be affected by the sample forms that have different surface areas. This tendency may be caused by high surface tension and low wettability of mercury against the polymer sample. It is desirable that a pillar sample is used for high-accuracy PVT measurement. Large error of specific volumes, however, will not be caused by using pellet sample. The PVT of the polycarbonate pillar are listed in Table II.

Correlation by Simha-Somcynsky Equation of State

The measured PVT in the equilibrium melt state were correlated using Simha and Somcynsky equation of state[22] as follows.

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{(y\tilde{V})^{1/3}}{(y\tilde{V})^{1/3} - y2^{-1/6}}$$

$$- \frac{2y}{\tilde{T}(y\tilde{V})^2}[1.2045 - 1.011(y\tilde{V})^{-2}] \quad (3)$$

where $\tilde{P} = P/P^*$, $\tilde{V} = V/V^*$, and $\tilde{T} = T/T^*$ are reducing variables and P^*, V^*, and T^* are characteristic parameters. A fraction of vacancies $(1 - y)$ can be obtained by solving eqs. (3) and (4), which are derived by a minimization of the Helmholtz free energy.

$$(s/3c)[1 + y^{-1}\ln(1 - y)]$$

$$= \frac{y/6\tilde{T}}{(y\tilde{V})^2}\left(2.409 - \frac{3.033}{(y\tilde{V})^2}\right)$$

$$+ \frac{2^{-1/6}y(y\tilde{V})^{-1/3} - \frac{1}{3}}{1 - 2^{-1/6}y(y\tilde{V})^{-1/3}} \quad (4)$$

P^*, V^*, and T^* were determined by correlating the PVT properties using a nonlinear least-squares fitting for each polymer. The correlation results of polypropylene and polycarbonate are shown by solid lines in Figures 8 and 9, respectively. The characteristic parameters and correlation errors are listed in Table III. Agreements between correlated and experimental results are excellent for both the polymers.

CONCLUSION

An apparatus for measuring the PVT properties of polymers has been developed for temperatures
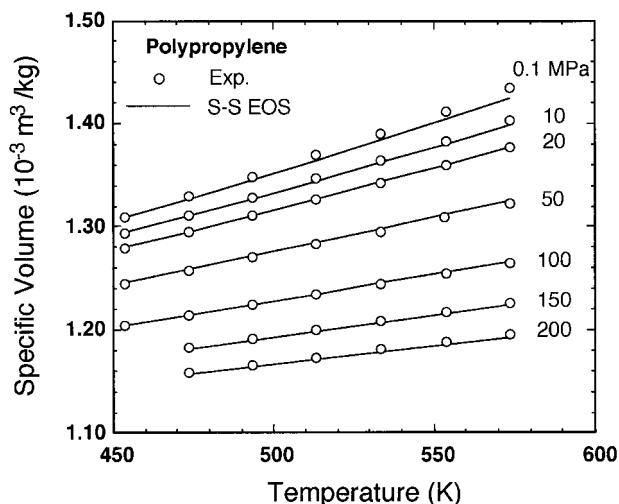
Figure 8 Correlation of PVT data for polypropylene in the melt state using Simha-Somcynsky EOS.

Table III   Correlated Parameters for the Simha-Somcynsky Equation of State

	P^* (MPa)	V^* (10^{-3} m³/kg)	T^* (K)	AAD[a] (%)
Polypropylene	547.9	1.1867	10924	0.16
Polycarbonate	948.9	0.8163	11955	0.08

[a] AAD = 100 ($\Sigma|v_{cal} - v_{exp}|/v_{exp}$) (1/$n$).
n = number of data.

from 313 to 623 K and pressures up to 200 MPa. PVT of polypropylene and polycarbonate was measured by the apparatus. The reproducibility of the measurements was within 0.1%. The differences of measurements with the sample cup and without the sample cup of both the polymers and an effect of sample forms (pellets and pillar) of polycarbonate on the PVT measurements were investigated. The differences of the sample cup have not had a clear effect on PVT properties. The experimental specific volume in the case of a pellet,
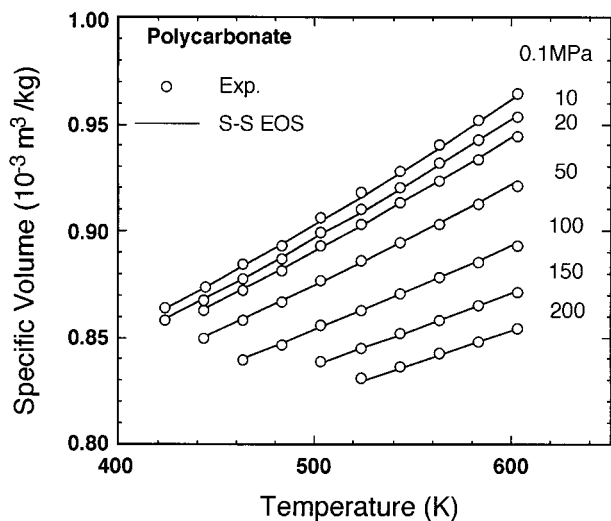
however, showed systematically a little higher value than that of the pillar under the low-pressure and high-temperature region. This tendency may be caused by high surface tension and low wettability of mercury against the polymer sample. It is desirable that the sample form of a pillar or a mass is used for high accuracy PVT measurement, although the effect of the sample form is not very much larger than the accuracy of the measurements.

The PVT data measured in the melt state were correlated using the Simha-Somcynsky equation of state, and the correlated PVT data are in excellently good agreements with experimental values.

Figure 9 Correlation of PVT data for polycarbonate in the melt state using Simha-Somcynsky EOS.

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