Simple Dilatometer for Polymer Density and Thermal Expansivity Measurements

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Synopsis

A dilatometer is described to study the temperature dependence of density (ρ) of solid and semiliquid polymers and the following linear relations have been established. Atactic poly(vinyl-isobutyl ether) (25–90°C): $\rho = 0.9166 - 7.15 \times 10^{-4} \times T$. Isotactic poly(vinylisobutyl ether) (25–70°C): $\rho = 0.9184 - 7.13 \times 10^{-4} \times T$. Poly($n$-butyl methacrylate) (90–150°C): $\rho = 1.0622 - 8.41 \times 10^{-4} \times T$. Poly(dimethyl siloxane) (30–51°C, using Lipkins pycnometer): $\rho = 0.9846 - 8.81 \times 10^{-4} \times T$; where ρ is in g.cm^{-3}, temperature T is in Celsius, and the linearity correlation coefficient r is better than 0.9998. Their volume–temperature plots are also linear. As the plots of poly(n-butyl methacrylate) curved slightly near its glass transition (20°C), the quadratic equation $\rho = 1.0402 - 4.79 \times 10^{-4} \times T - 1.46 \times 10^{-6} \times T^2$ (standard deviation = 1.57×10^{-3}) has been suggested for the entire range of 30–150°C scrutinized in this study. The data have been utilized to derive thermal expansivity and some equation-of-state parameters of the polymers at the reference temperature (ca. 20°C).

INTRODUCTION

Density measurements afford a very sensitive means of characterizing the temperature dependence of the properties of condensed matter. They form the basis for the derivation of volumetric expansion and equation-of-state data on pure substances, which are essential for (statistical thermodynamic) interpretation of the properties of mixtures and solutions and for establishing correlations between thermal and mechanical properties of substances. Since polymers are characterized by low coefficients of thermal expansion and of compressibility, their study acquires special significance. However, thermal expansivity data of the required accuracy over a sufficiently wide temperature range are available for only a small number of common polymers (e.g., Refs. 2–9).

In certain situations, such as analytical and nonanalytical uses of polymeric stationary phases in gas chromatography,[1,10-12] the density, and occasionally even the equation-of-state data, are desired both at ambient and some higher range of temperature. As the polymers used in these applications happen to be mostly new, their densities have to be measured experimentally. Among several methods available for this purpose (c.f. see brief reviews in Refs. 9, 13, and 14), pycnometry is preferred for low-molecular-weight liquids at temperatures normally below 100°C while the volume dilatometry (displacement of a standard confining fluid like mercury in a capillary by the sample) is capable

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of determining volume change in both liquids and solids due to thermal expansion directly or even continuously over higher ranges.[3-9,11,13,14]

Since the review of Bekkedahl[13] on the design and use of volume dilatometers, there have been only a few developments in this area. For example, Laub and Pecsok[11] have described a simple dilatometer to measure densities of liquids from at least 0° to 300°C offering better accuracy than common pycnometers, and some advantages over other dilatometers. Yet special attention is needed during the "filling" of the dilatometer to prevent micro air bubbles from being trapped near the stopcocks, in the sample and in mercury; also the weight of sample and mercury is determined by an indirect method. Höcker et al.[7] have designed a dilatometer for precise measurements with solid samples over wide temperature ranges, which can also be used for thermal pressure coefficient measurements. However, their procedure becomes cumbersome and time consuming, especially when temperature is raised in small steps over a wide range, in addition to the requirement of large quantity of sample, which may not be available in many instances. More sophisticated densitometers such as that recently devised by Craubner[9] need very small amounts of sample and can yield extremely accurate values of absolute as well as relative densities of solid and liquid substances from subzero to elevated temperatures. In any event, these devices are too intricate and often too expensive to be used in small laboratories or where expedience is a criterion for the measurements.

With these several considerations in mind, and specially prompted by the necessity to furnish density and equation-of-state data for atactic and isotactic poly(vinylisobutyl ethers) and poly(n-butyl methacrylate) at various temperatures required in our previous gas chromatographic investigations,[1] which appeared not to have been carried out hitherto, a simple dilatometer was constructed, that was easy to use and capable of high precision and accuracy for both solid and viscous samples from at least 0° to 200°C. That apparatus has been described in this communication, and the results are presented. The density of poly(dimethyl siloxane) was measured (by a Lipkins pycnometer) because the molecular weight and polydispersity of our sample[1] differed widely from those for which the data are available in the literature.[3-5,8]

EXPERIMENTAL

Materials

Poly(n-butyl methacrylate) (PnBMA) was prepared by free radical polymerization at 70°C using benzoyl peroxide as the initiator dispersed in toluene.[15] Atactic and isotactic poly(vinylisobutyl ethers) (PVIBE) were obtained by cationic polymerization, respectively, at ambient temperature and at −40°C.[15,16] The polymer samples were reprecipitated twice from benzene solution by adding methanol and were dried in a vacuum oven at 50°C for several days. Poly(dimethyl siloxane) (PDMS) was a product of Metroark (India) Ltd. and had a viscosity of 100 cst; it was used as received. The number-average molecular weight ($\overline{M}_n$) of polymer was estimated by using Knaur vapor pressure and membrane osmometers, and the viscosity-average molecular weight ($\overline{M}_v$) by determining the intrinsic viscosity [η] in dilute

TABLE I
Polymer Properties and Constants for Mark-Houwink-Sakurada Equation[a, b]
$$[\eta] = K(\overline{M}_n)^a$$

nPolymer	$K \times 10^{-3}$ (ml g^{-1})	a	$[\eta]$ (ml g^{-1})[c]	$\overline{M}_v$	$\overline{M}_n$
aPVIBE[a]	7.55	0.75	6.7	8600	2340
iPVIBE[a]	7.55	0.75	8.9	12,400	2500
PDMS[b]	21.50	0.65	9.2	11,250	3060
PnBMA[a]	4.00	0.77	77.9	372,000	91,300

[a] PVIBE-Ref. 16; PnBMA-Ref. 2; solvent is benzene and temperature is 30°C.
[b] PDMS-Ref. 2; solvent is toluene and temperature is 25°C.
[c] Standard error ≈ 1%.

solutions, Table I. The glass transition temperature of PnBMA was measured with a home-built thermomechanical analyzer, and was found to be 18 ± 2°C.

Dilatometry

Figure 1 shows the schematic diagram of the all-glass density apparatus. It includes a U-shape sample tube AB closed at A, a uniform bore capillary BC, and a filling device CG. Three pairs of "Quickfit" greaseless and leak-proof ground glass joints have been provided at B, and C, and G to join the three sections together and to a vacuum system. For polymer dilatometry mercury is considered to be the best confining fluid because of the availability of accurate density data for this substance over a wide temperature range and its inertness for most polymers.[7,14] It has been employed, therefore, to calibrate the present dilatometer. The dimensions of the appartus are not critical; however, we found that the parameters given in Figure 1 were the most useful size, allowing an accurately measurable rise of mercury meniscus in the capillary for most polymer samples without requiring an excessive length of the capillary. The bulb D was used to store purified mercury and was provided with a narrow bore tube that would facilitate to pour mercury directly into the capillary and would also prevent backflow into the bulb as well as contamination. The second bulb E was used to collect mercury drained from the apparatus. The bulbs were positioned at different heights, aligning at approximately a 45° angle with each other, on the same side of the filling device. This spatial arrangement, reached after trial and error, proved to be beneficial for operational convenience. A constriction F further prevented accidental spill from the dilatometer as well as guarded the contents against external contamination.

The dilatometer was first thoroughly cleaned and dried. Then, approximately 0.5–1 g polymer sample was placed at the bottom of the preweighed sample tube. To ensure that the sample was free from trace volatile matter (such as residual monomer, initiator, solvent, and water), the loaded tube was dried in a vacuum system (at 10^{-6} Torr and 50°C) until constant weight was achieved. (Solid samples were cut into very thin slices to expose the "voids" and to provide larger surface area for vacuum drying.) The bulb D was filled with 8 to 10 mL of mercury. The apparatus ABCG was then assembled and attached to a high vacuum system for degassing. To dislodge microbubbles of
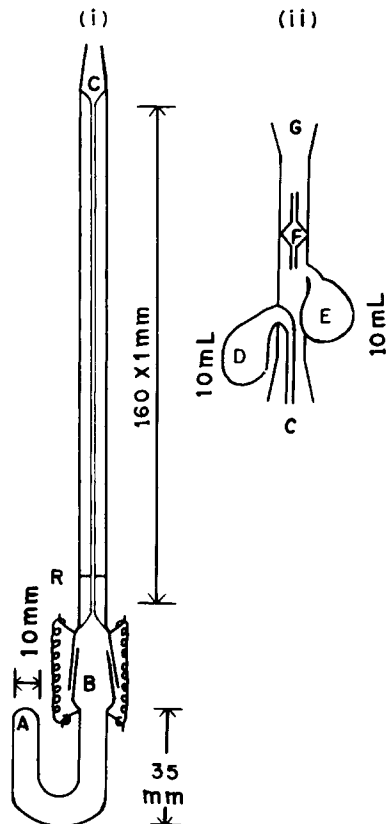
Fig. 1. Schematic diagram of (i) dilatometer and (ii) vacuum "filling" device described in the text.

air from mercury it was found advantageous to shake the bulb gently and dip it alternately in warm and cold water a few times. After satisfactory degassing, mercury was allowed a free fall from the bulb D into the sample tube AB through the capillary BC by tilting the apparatus in order to trap the polymer sample at the closed end A and to fill the apparatus simultaneously. (It should be mentioned that an apparent void observed over mercury at A when the vacuum was maintained at C, was completely occupied by mercury after the upper end of the capillary was open to the atmosphere. However, it necessitated that a mercury column approximately 10 cm in height was maintained above the fixed reference mark R before breaking the vacuum.) The excess mercury, if any, was withdrawn into the bulb E by appropriate maneuvering of the apparatus before disconnecting it from the vacuum line. The filling device was then detached from the dilatometer; the difference in its weight before and after the "filling" process was taken as the mass of mercury loaded in the dilatometer ABC. The pressure difference between A and C was considered to be sufficient to forcibly immerse the sample into mercury and to fill all void spaces in the system. The dilatometer was subsequently transferred to a glass-wall thermostat immersing the full length

of capillary in the bath fluid (leaving only the upper end of $\underline{C}$ out); the temperature was precisely regulated and read to the accuracy of $\overline{0.05}°C$.

The height $\underline{H}$ of mercury meniscus in the capillary was measured by a cathetometer to the accuracy of 0.01 mm with respect to the reference mark $\underline{R}$ under isothermal conditions. The system was allowed to attain thermal equilibrium for at least 5 h after the set temperature was reached. The measurements were repeated until at least five consecutive readings were reproducible over a period of 2 h in order to provide a reliable value. This value was then used to determine the combined (total) volume V (cm^3) of the polymer sample and mercury in the dilatometer from the following relation that was established in a separate but identical experiment (calibration) in which the dilatometer was filled up only with mercury and the meniscus height was recorded at close intervals of temperature in the range 25–150°C.

$$V = 4.39405 + 1.14539 \times 10^{-3} \times H - 7.97702 \times 10^{-10} \times H^2$$

The volume of mercury V_{Hg}(cm^3) was calculated from its mass and density.[17] Similarly, the polymer density ρ(g cm^{-3}), hence specific volume ν (cm^3 g^{-1}), was determined from its mass W (g) since,

$$\rho = \nu^{-1} = W/(V - V_{Hg})$$

Upon reversing the temperature cycle, the density values were found to be reproducible to 0.0002 g m^{-3}.

The density of PDMS was measured at different temperatures from 30° to 51°C following the standard procedure with a precalibrated Lipkins pycnometer.

The data reduction was carried out by multiple regression method of least-squares to determine the temperature coefficients of density and specific volume and their random errors. The results are summarized in Tables II and III.

RESULTS AND DISCUSSION

Density

Figure 2 shows that, in general, the polymer density decreases linearly with temperature in the range studied according to equation:

$$\rho = a' + b'T$$

The linear least-squares intercepts a' and slopes b' for all polymers are given in Table II. Also shown in this table are the correlation coefficients r, standard errors SE (estimated to be less than 0.1% in intercepts and 1% in slopes), and predicted densities for each polymer at 25°C (precise to the fourth decimal and in good agreement with the reported data that are considered to be the best or in intermediate range available in literature[2,4,7,14,18]). Taken together, they demonstrate the goodness of the linear regression at the indicated temperatures with one exception.
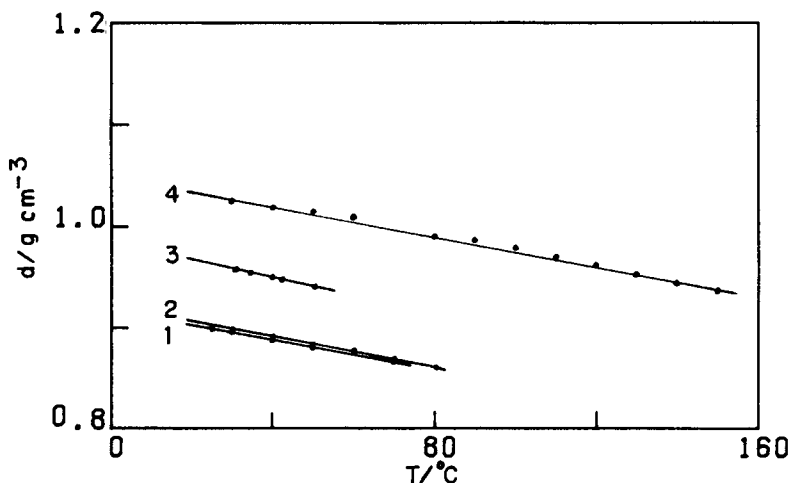
Fig. 2. Temperature dependence of density for aPVIBE (1), iPVIBE (2), PDMS (3), and PnBMA (4).

The plot of PnBMA, though truly linear at temperatures above 90°C ($r = 0.9999$), turns out to be only approximately linear as the temperature is lowered to its glass transition (r degenerates to 0.9968 while SE moves up 2–3 times). The quadratic equation provided in the footnote of Table II has been derived, therefore, to account for the (anticipated) deviations in the temperature coefficient of density since the range (temperature) covered in this case is wide. It may, however, be noted that the polynomial regression has altered the predicted density values by no more than 0.4% as compared to the linear regression method, the difference being much smaller and within experimental error for other polymers. Some experimental scatter evident in the data is partly responsible for this deviation. Thus, the use of linear regression is justified unless precision in higher order terms of the above equation is required in which case the quadratic equation must be preferred.

Specific Volume

The specific volume–temperature plots of polymers were also linear except the curvature in PnBMA plot, now clearly visible with decreasing temperature close to the glass transition. Table III lists the least-squares intercepts a'', slopes b'', correlation coefficients r, and standard errors for the linear dependence ($v = a'' + b''T$). To account for small deviation from linearity in case of PnBMA, we have worked out a quadratic equation for the entire temperature range studied (see footnote in Table III). It is inferred from the results that the volumetric expansion coefficient of PnBMA may be treated independent of temperature from at least 90° to 150°C. Thus support is provided to the general view that the thermal expansivity is not exactly independent of temperature, but normally should show a gradual increase with temperature particularly if the range (temperature) covered is very large. (Common practice, however, is to report thermal expansivities of solid polymers assuming linear dependence of volume on temperature immediately below and above

TABLE II
Constants for Density-Temperature Relation ρ (g cm^{-3}) = $a' + b'T$(°C),[a] and Densities at 25°C

Polymer	Temperature °C	Intercept		-Slope × 10^4		Correlation	ρ (g cm^{-3}) at 25°C	
		a'	SE	$-b'$	SE	r	Predicted	Literature
aPVIBE	25–90	0.9166	0.0003	7.15	0.05	0.9999	0.8987 ± 0.0002	0.91–0.92[c]
iPVIBE	25–70	0.9184	0.0004	7.13	0.07	0.9998	0.9005 ± 0.0002	0.91–0.92[c]
PDMS	30–51	0.9846	0.0004	8.81	0.09	0.9998	0.9626 ± 0.0002	0.9682[b]
PnBMA[a]	90–150	1.0622	0.0008	8.41	0.06	0.9999	1.0412 ± 0.0007	1.055[c]
	30–150[a]	1.0497	0.0019	7.39	0.19	0.9968	1.0312 ± 0.0014	

[a]The corresponding quadratic equation for PnBMA (30–150°C): ρ = (1.0402 ± 0.0026) − (4.79 ± 0.66) × 10^{-4} × T − (1.46 ± 0.36) × 10^{-6} × T^2, correlation coefficient = 0.9978; SE = 1.55 × 10^{-3}; ρ(25°C) = 1.0273 g cm^{-3}.
[b]Ref. 4
[c]Ref. 18.

TABLE III
Constants for Specific Volume-Temperature Relation ν $(cm^3\ g^{-1}) = a'' + b''T(°C)^a$

Polymer	Temperature °C	Intercept a''	SE	Slope $\times 10^4$ b''	SE	Correlation r
aPVIBE	25–90	1.0890	0.0005	9.33	0.09	0.9997
iPVIBE	25–70	1.0875	0.0004	9.11	0.09	0.9998
PDMS	30–51	1.0143	0.0004	9.63	0.09	0.9998
PnBMA[a]	90–150	0.9313	0.0013	9.10	0.11	0.9997
	30–150[a]	0.9489	0.0024	7.68	0.24	0.9949

[a] The corresponding quadratic equation for PnBMA (30–150°C): $\nu = (0.9625 \pm 0.0026) + (3.95 \pm 0.65) \times 10^{-4} \times T + (2.09 \pm 0.36) \times 10^{-6} \times T^2$; SE $= 1.55 \times 10^{-3}$; correlation coefficient $= 0.998$.

glass transition; that procedure has been followed to derive equation-of-state parameters in this study too.)

Equation-of-State Parameters

When the system is in equilibrium the equation-of-state describes the dependence of the volume on the state variables independent of the past history of sample. For polymers only the melt and the solution states are anywhere closer to the ideal or true equilibrium state for which the properties of the equation of state are commonly expressed in the form of the following derivatives.[7,8,19]

$$\alpha = \nu^{-1}(d\nu/dT)_P = -\rho^{-1}(d\rho/dT)_P$$

$$\nu^* = \nu\left[1 + \{\alpha T/3(1 + \alpha T)\}\right]^{-3}$$

$$\tilde{\nu} = \nu/\nu^*$$

$$T^* = T\left[\tilde{\nu}^{4/3}/(\tilde{\nu}^{1/3} - 1)\right]$$

$$\tilde{T} = T/T^*$$

where ν is the specific volume, α is the coefficient of cubic thermal expansion; T is the absolute temperature; tilde ($\sim$) and asterisk($*$) denote, respectively, the reduced and hard core parameters. For PnBMA, determination of these quantities is complicated by the fact that the polymer is a glass at ordinary temperatures, whereas ν and α for the liquid, as opposed to the glass, are required for evaluation of the equation-of-state parameters specified by the theory. Hence, the usual procedure has been applied to the determination of the specific volume and the thermal expansion coefficient of liquid polymer at equilibrium as recommended by Höcker et al.[7] That is, the data much above its glass transition temperature ($\sim$ 20°C) were extrapolated to the reference temperature ($\sim$ 20°C), in this case linearly. As other polymers were viscous fluids at this temperature and their volume–temperature plots were linear, there was no difficulty in this regard. The specific volume ν $(cm^3\ g^{-1})$ instead

TABLE IV
Some Equation-of-State Parameters at 20°C Determined by Linear Regression
of Polymer Density Data (Table II)

Polymer	v (cm^3 g^{-1})	$\alpha \times 10^3$ (K^{-1})	$\tilde{v}$	$\tilde{T} \times 10^2$	T^*(K)	v^* (cm^3 g^{-1})
aPVIBE	1.1083	0.7922	1.2007	4.926	5951	0.9230
iPVIBE	1.1061	0.7885	1.1998	4.909	5972	0.9219
PDMS[a]	1.0341	0.9110	1.2259	5.355	5475	0.8435
	(1.0265)	(0.9065)	(1.2248)	(5.34)	(5494)	(0.8381)
PnBMA	0.9663	0.7142	1.1833	4.611	6358	0.8166

[a] The data in parentheses are reproduced from Ref. 8 ($\bar{M}_v \approx 10^5$) for comparison.

of the molar specific volume v_{sp} (cm^3 mol^{-1})($= M/\rho$) was chosen for these calculations because of the vague definition of polymer molecular weight (M). The results thus obtained for each polymer are given in Table IV. We found α for PDMS at 20°C as 0.9110×10^{-3} (K^{-1}). Allen et al.[6] reported $\alpha = 0.90 \times 10^{-3}$ (K^{-1}) for PDMS of mol wt ≈ 15000; and Shih and Flory[8] determined $\alpha = 0.9056 \times 10^{-3}$ (K^{-1}) for PDMS of $\bar{M}_V \approx 10^5$. The equation-of-state parameters for PDMS from Ref. 8 are reproduced in parentheses in Table IV for comparison.

The experimental results demonstrate that the new apparatus can be employed at both low and high temperatures outside the range mentioned above by use of appropriate technical means. The sensitivity of the apparatus to monitor small variations in polymer-volume with temperature is good and may be altered further by merely changing the sample amount and/or the bore of capillary.

In conclusion, the new dilatometer is simple to construct, convenient to operate, and inexpensive to use. It allows repetitive measurements by reversing the temperature cycle as many times as permitted by the thermal stability of the sample. The unique vacuum "filling" procedure eliminates some and reduces many sources of common errors in these measurements. Calibration of mercury in the present manner eliminated a number of variables or at least reduced the corrections to negligible, for example those otherwise necessary due to the volume change of the U-section and the length of the capillary during heating. It is expected that this dilatometer will also be suitable for nonpolymeric solids and semiliquid substances.

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