Volumetric properties of polystyrene: influence of temperature, molecular weight and thermal treatment

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Specific volumes (v) of a series of anionic polystyrenes (M = 2000 to 2 000 000) have been measured dilatometrically over the temperature range −30° to 210°C. General equations are given for v as a function of temperature and molecular weight and are used to calculate glass temperatures and free volumes.

INTRODUCTION

The glass temperature (T_g) of a polymer is that temperature at which there is a sudden change of slope in the specific volume–temperature curve. T_g is therefore conventionally obtained by dilatometry but this is a time consuming process and we are at present developing a rapid calorimetric procedure for the accurate determination of T_g since specific volume can be replaced by enthalpy or any other extensive thermodynamic quantity. For comparative purposes it is important to have an independent set of reference values and in this paper we report dilatometric T_g values for a series of well defined polystyrenes. Although dilatometry is most often used as a relative technique (changes in specific volume are sufficient to define T_g) the extra effort needed to obtain absolute specific volumes is well worthwhile since there is considerable scatter in existing values and, as polymers find use in increasingly demanding situations, it is important that reliable data are available. The specific volumes reported here are used to discuss how the free volume is affected by molecular weight and thermal treatment.

EXPERIMENTAL

Polymers

Anionic polystyrenes were supplied by the Pressure Chemical Co., Pittsburgh (*Table 1*); in general $M_w/M_n < 1.1$ although this may rise to 1.3 for the highest *MW*. When properties were only slowly varying functions of *MW* ($M > 20\,000$) the *MW* data supplied by the manufacturer were used. Lower values were checked in this laboratory and the results are shown in *Table 1*. The only significant disagreement is for sample 11b where the Pressure Chemical Co. data are themselves at variance, our osmometry measurements used cellulose acetate membranes and as no decrease in osmotic head was noted over 1 h we are condident there was no diffusion of polymers through the membrane.

Polymer was a fine powder or floc and was used as received, residual solvent or volatile materials being pumped off in the dilatometer prior to filling with mercury (see below).

Dilatometry

All experiments were carried out in sealed, all-glass dilatometer using mercury as the confining liquid. Dilatometers were loaded by pouring the polymer powder into the weighed, unsealed vessel (*Figure 1*) prior to sealing at A

Table 1 Molecular weight data for polymers investigated

Batch no.	*MW* (Pressure Chemical Co.)	*MW* (NPL)
16a	580*	–
12b	2050–2210*	2050
11b	3100*	3660
8b	9600–10 000*	10 400
2b	20 200	19 800
7b	36 000	–
4b	111 000	–
1c	193 000	–
13a	640 000	–
14b	1 999 000†	–

All are M_n via membrane osmometry except where indicated: *vapour pressure osmometry; †intrinsic viscosity

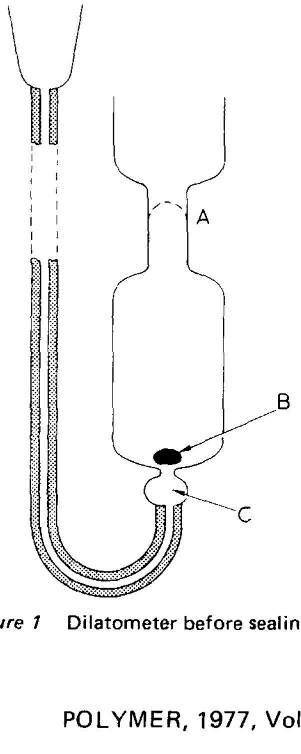

Figure 1 Dilatometer before sealing at A

and weighing the glass removed. The pellet B ensured that only a small amount of powder entered the capillary region and this was easily returned to the bulb C prior to degassing. The overall density of the higher molecular weight material was very low so that frequent tamping was needed in the loading operation. Dilatometers typically contained 5 g of polymer which occupied between 30 and 50% of the available volume.

All polymers contained a small (<1%) amount of volatile material which was removed by pumping on the *inverted* dilatometer until the pressure was less than 10^{-4} mmHg and then slowly raising the temperature to about $T_g + 50°C$. The lower molecular weight material foamed considerably at this stage and the small bulb C was found to be very effective in preventing bubbles entering the capillary region. After 2 h the molten polymer was allowed to cool under vacuum to room temperature and the dilatometer plus polymer reweighed. This process was then repeated to ensure that all volatiles had been removed. Finally the dilatometer was filled under vacuum with mercury in the usual way[1].

The above procedure gave accurate weights (buoyancy corrections were always applied) of glass, mercury, and polymer but not the specific volume of the last since the total volume of the dilatometer was unknown. At the end of all measurements on a given polymer, therefore, the dilatometer was emptied by repeated leaching with chloroform and refilled with mercury alone to give the total volume. Occasional calibration runs were also made with mercury over the whole temperature range and these confirmed the figure of 10^{-6} [2] for the coefficient of cubical expansion of pyrex glass.

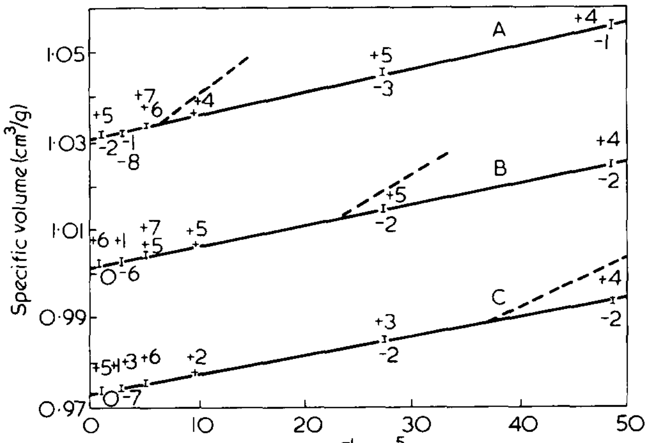

Figure 2 The specific volume of molten polystyrene according to equation (2). Numbers show the deviations (in cm³/g × 10⁴) of independent experiments from this line. ———, Show schematically how the suggested T_{ll} transition behaves (see text) so that for M_n with T_{ll} in the range shown there should be an increased deviation at the highest temperatures. A, 200°C; B, 150°C; C, 100°C

Measurements were made over the temperature range −35° to 210°C by immersing the dilatometer in methanol (to 10°C), water (to 70°C) or silicone oil baths which were maintained at temperatures constant to ±0.05°C (methanol) or ±0.01°C (water, silicone oil). Temperatures were read to ±0.01°C using mercury-in-glass thermometers calibrated in this laboratory. The position of the mercury meniscus in the 1 mm precision bore capillary tube was read to ±0.001 cm using a cathetometer. The capillary was calibrated with mercury in the usual way. All calculations used Bigg's data[3] for the density of mercury.

Procedure

Measurements were made in the following sequence: liquid, glass (g_1), liquid, glass (g_2), glass (g_3) etc., where the symbols g_1, g_2, etc. refer to the various thermal treatments which were used to produce the glass, the most common method was to cool from $T_g + 20°C$ to $T_g - 20°C$ at 2.5°C/day. Only one or two random checks of liquid specific volumes were needed in between measurements on glasses g_2 and g_3 since it was invariably found that for a given dilatometer reproducibility of results in the liquid state was such that any deviation from a smooth curve was less than $\pm 10^{-4}$ cm³/g.

RESULTS

The experimental precision was such that only very large scale figures can adequately display our results (see *Figure 2*) and specific volumes are therefore given in *Table 2* as quadratic functions of temperature, the quadratic form is adequate for all samples in both the glassy and liquid state with the exception of the lowest molecular weight oligomer for which the liquid must be represented by a cubic (no measurements were possible for the glass since $T_g \simeq -30°C$, near the minimum temperature attainable with mercury dilatometers). The parameters of *Table 2* are based on data which cover the approximate ranges −35°C to $T_g - 15°C$ and $T_g + 15°C$ to 210°C for the glassy and liquid states, respectively. Experiments were frequently repeated (i.e. new samples prepared in new dilatometers) especially with low molecular weight material and *Table 2* incorporates data from three independent experiments on both M_n = 2050 and 3660. The maximum deviation from the average

Table 2 Volumetric parameters and glass temperatures of polystyrene

	$v_g = a + bT + cT^2$ (cm³ g⁻¹, °C)			Glass temperature (°C)		$v_l = A + BT + CT^2$ (cm³ g⁻¹, °C)		
M_n	a	$b \times 10^4$	$c \times 10^7$	T_{go}	T_{gs}	A	$B \times 10^4$	$C \times 10^7$
2050	0.9510	2.129	2.297	44.0	44.5	0.9356	5.619	2.135
3660	0.9500	2.053	2.198	64.7	64.9	0.9282	5.426	2.144
10400	0.9501	2.006	2.470	85.0	83.1	0.9217	5.412	1.687
19800	0.9501	1.988	1.424	86.1	87.9	0.9214	5.278	1.941
36000	0.9504	1.980	1.388	91.5	90.4	0.9199	5.276	1.792
111000	0.9501	1.965	1.577	93.2	92.5	0.9192	5.255	1.806
193000	0.9497	1.940	1.883	93.0	92.9	0.9194	5.188	2.002
640000	0.9500	1.956	0.982	91.9	93.3	0.9183	5.344	1.601
1990000	0.9499	1.966	2.193	95.2	93.4	0.9198	5.106	2.459
580	$v_l = 0.9763 + 6.692 \times 10^{-4}T + 3.77 \times 10^{-8}T^2 + 1.127 \times 10^{-9}T^3$; $T_g \approx -30°C$							

Glass temperatures are solutions of the equation $v_g = v_l$ using either the above parameters (T_{go}) or equations (1) and (2) (T_{gs})

parameters of *Table 2* was 10×10^{-4} cm^3/g in the glassy state and 7×10^{-4} cm^3/g in the liquid state. Results are less good for the glass since even for a given sample reproducibility was poorer than for the liquid. Thus a well annealed glass which was never heated above $\sim T_g - 15°$C gave a volume–temperature curve which was reversible, data reproducing to better than $\pm 10^{-4}$ cm^3/g, as with the liquid, but when attempts were made to reproduce the same glass from the melt (i.e. $g_2 \equiv g_1$) differences of up to 3×10^{-4} cm^3/g were found and these are further considered in a later section when we discuss the overall experimental accuracy.

Only superficial attention has been paid to the transition region ($T_g \pm 15°$C) itself since here rate effects are very important. These have been extensively discussed by Kovacs[4]. In this work we seek 'equilibrium' data – an expression which we feel may justifiably be applied to our well annealed glasses by virtue of the reversibility of their volume–temperature curves.

DISCUSSION

Transitions

Transitions have been reported in both the glassy and liquid states in the temperature range encompassed by our measurements. It is therefore very important to see what information our results give about such transitions since any subsequent discussion will of necessity be influenced by their nature and magnitude.

Dynamic test methods show that polystyrene has a β-transition at ~50°C but only Goldbach and Rehage[5] have reported a corresponding effect on the volume–temperature curve. They found an abrupt change of ~10% in the expansivity ϕ ($=\partial v/\partial T$) which was otherwise independent of temperature in this region. Our results, which cover a wider range of temperature, indicate that ϕ changes smoothly with temperature and there is no obvious discontinuity at 60°C, which is where we estimate T_β should be for our particular thermal treatment. However 60°C is approaching the limit for 'pure' glassy data since ~15°C above this ϕ_g comes under the influence of the glass transition and starts its climb to ϕ_l. The best conditions for the volumetric observation of T_β are clearly in quenched samples where T_β is lowered[5] and T_g is increased[6]. For our experimental conditions T_β may be undetectable because not enough high temperature data can be obtained to define a discontinuity in the ϕ–temperature curve.

By contrast with T_β, which is a well understood phenomenon (albeit having little effect on the volume–temperature curve) the suggested liquid–liquid transition (at a temperature T_{ll}) is considerably more controversial. Boyer[7] has reviewed evidence for what appears to be the onset of motion on a whole molecule, as opposed to segmental, scale. Among the evidence cited is the dilatometric work of Fox and Flory[8] who observed that their results for the liquid could be equally well represented by two intersecting (at T_{ll}) straight lines or a single smooth curve. More recent work by Höcker, Blake and Flory[9] has shown that α ($= \partial \ln v/\partial T$) is a continuous function of temperature throughout the range 100°–220°C. Our results are in very good agreement with theirs; absolute values of specific volumes (after correcting to the $M_n = 51\,000$ of ref 9) agree to 0.0005 cm^3/g and in both cases α(150°C) $= 5.81 \times 10^{-4}$ °C^{-1}. There may be a change of slope at ~170°C in the α–T curve of Höcker *et al.* but there is no discontinuity (as would be the case with intersecting straight lines) and none is visible in our results – a clear indication that, whatever the nature of the transition, it is not detectable dilatometrically.

Further evidence is provided by the behaviour of specific volume curves as functions of molecular weight. As M increases so, it is suggested[10], does T_{ll}. Hence if we plot v_l against $1/M$ at a series of increasing temperatures we would anticipate that each isotherm $T_1 \ldots$ etc would have a discontinuity (shown schematically by the broken lines in *Figure 2*) at that value of M for which $T_{ll}(M) = T_1$ and this will shift to higher values of M for $T_2 > T_1$. *Figure 2* shows no effect of this type is discernible at 100°, 150°, or 200°C. Indeed if, for a given M, we note the differences between the experimental and regression analysis values (equation 2, below) we find that this is essentially constant between 100° and 200°C and for M_n from 2×10^3 to 2×10^6 which suggests consistent (for a given experiment) but random (from one sample to another) experimental errors. The numbers inserted on *Figure 2* illustrate this point, for example data for one sample of $M_n = 2050$ were consistently in error by $+4 \times 10^{-4}$ cm^3/g and for $M_n = 193\,000$ by +6 or $+7 \times 10^{-4}$ cm^3/g showing that a single curve is adequate to describe the behaviour of the liquid.

We conclude that, at least for monodisperse polystyrenes, volumetric data cannot be used in support of the concept of a liquid–liquid transition.

Generalized equations

It is clear from *Table 2* and *Figure 2* that v_l is a function of M_n^{-1} but the corresponding relationship for v_g is less obvious. To a large extent our results confirm Fox and Flory's original suggestion[8] that v_g is independent of M but this is certainly not true when $M_n = 2050$ and, as we wish to generalize our results over as large a range of M as possible, we shall treat both v_g and v_l as functions of M as well as temperature.

Results for individual polymers immediately suggest that a general equation should have the form:

$$v = A + BT + CT^2 + (a + bT + cT^2)/M$$

and our results were initially fitted in this way using a multiple regression analysis. The resulting parameters indicated that the constant c could be omitted with very little loss of accuracy; for the glass c is small and of opposite sign to a and b; for the liquid, although a, b and c are all positive, the quantity $\phi(T_2) - \phi(T_1) = 2C(T_2 - T_1) + 2c(T_2 - T_1)/M$ is essentially independent of M i.e., $c \simeq 0$. By contrast b cannot be neglected since, when $c = 0$, $\phi = B + 2CT + b/M$ and for both phases ϕ increases by ~8% in the range $M = 2 \times 10^6$ to 2×10^3. The final curve fitting gave the equations:

$$v_g = 0.9498 + 1.962 \times 10^{-4}\,T + 1.683 \times 10^{-7}\,T^2 + (3.157 + 3.229 \times 10^{-2}\,T)/M \quad \text{cm}^3\text{g}^{-1}, °\text{C} \qquad (1)$$

$$v_l = 0.9199 + 5.098 \times 10^{-4}\,T + 2.354 \times 10^{-7}\,T^2 + (32.46 + 0.1017\,T)/M \quad \text{cm}^3\text{g}^{-1}, °\text{C} \qquad (2)$$

The *maximum* deviation of *any* result for *any* $M > 2000$ from equation (2) was 8×10^{-4} cm^3/g and was usually less than half of this.

Table 3 Comparison of data for polystyrene ($M = \infty$)

				Expansion coefficient ($\times 10^4$)			
		Specific volume (cm^3/g)		$\phi = \partial v/\partial T$ (cm^3/g °C)		$\alpha = \partial \ln v/\partial T$ (°C^{-1})	
Ref	Preparation*	Glass (30°C)	Liquid (100°C)	ϕ_{30}	ϕ_{100}	α_{30}	α_{100}
11	t	0.9578	0.9689	1.84	5.5	1.92	5.68
8	t	0.9505	0.9680	2.5	5.5	2.63	5.68
12	t	0.9508/18	0.9688	2.27	5.60	2.39	5.78
5	t	0.9552/5	0.9769	2.2	6.0	2.31	6.14
9†	a	–	0.9738	–	5.60	–	5.75
13	a	–	0.9781	–	4.67	–	4.77
This work	a	0.9558	0.9732	2.06	5.57	2.16	5.72
				2.26 (90°C)	6.04 (200°C)	2.34 (90°C)	5.86 (200°C)

*t/a = thermal/anionic polymerization; †reduced to $M = \infty$ via equation (2)

Equation (2) has already been used in a predictive role to compare our results with those of ref 9. In the range 100°–200°C results from equation (2) are 0.0006 cm^3/g below those of ref 9 while in the same range equation (2) indicates that α_l increases from 5.74 to 5.87×10^{-4} °C^{-1} compared with the observed change from 5.77 to 5.85×10^{-4} °C^{-1}. A critical test of the generality of equation (2) is in calculating the volumetric behaviour of the oligomer of degree of polymerization 6 ($M_n = 580$). Here there is almost exact agreement with observed values at room temperature but the initial temperature coefficient is too large and the predicted and experimental values diverge to a maximum of 26×10^{-4} cm^3/g at 150°C, above this temperature the observed curvature increases (as reflected in the cubic term, *Table 2*) and the difference falls to 17×10^{-4} cm^3/g at 200°C. Thus even for this lengthy extrapolation (equation 2 is based on results in the range $M_n^{-1} \simeq 0$ to 4.8×10^{-4}, $580^{-1} = 17.2 \times 10^{-4}$) the maximum deviation that equation (2) predicts from observed value is less than 0.25% whilst within the experimental range of M there is near quantitative agreement not only with v_l but also with the derived quantity, the expansion coefficient α_l.

A full comparison of our results, as given by equation (1) and (2) with existing data is given in *Table 3*. All values refer to infinite molecular weight, the original samples either approximated to this or an extrapolation is possible. Under these circumstances chain end effects should be negligible and the difference of about 0.005 cm^3/g between the specific volume of anionic and thermally polymerized polystyrenes may be due to differences in stereoregularity[9]. Although specific volumes themselves may depend on polymerization conditions it is clear that the expansion behaviour shows only trivial differences. $(5.7 \pm 0.1) \times 10^{-4}$ °C^{-1} covers nearly all data for α_l, and this increases by only 1 or 2% at 200°C, by contrast ϕ_l increases by ~8% in the same temperature interval (*Table 3*). There is considerably more scatter in the data for the glassy state and we will consider this in more detail in the following sections.

Although equations (1) and (2) are simply mathematical devices for the accurate representation of our experimental results and have no status as fundamental equations of state, they do indicate the kind of behaviour that the latter should predict and in this respect current theories cannot reproduce the observed behaviour using an unique set of reduced variables. This is most easily seen in the disparity between actual and calculated values of $\mathrm{d}\alpha/\mathrm{d}T$[9]. In the range 100° to 200°C, for example, α_l should increase by 12.6[14], 15.4[9] or 6.2%[15] compared with the observed 1 or 2% (ref 9, equation 2) so that theoretically based extrapolations may be subject to large uncertainties.

Errors

The generalized equations (1) and (2) form a basis for discussion of the experimental reproducibility and overall accuracy. Restricting our initial comments to the liquid state, the standard deviation of seventeen independent experiments from equation (2) is 5×10^{-4} cm^3/g. Excellent though this is with respect to, say, the spread of values in *Table 3* it should in theory be considerably better as dilatometry involves only the measurement of mass, length and temperature and for our conditions better than 10^{-5} cm^3/g should be attainable. At first sight the major restriction is the temperature stability of ±0.01°C, fluctuations in the mercury level were observable which paralleled such temperature changes but these only corresponded to uncertainties of $(1–2) \times 10^{-5}$ cm^3/g. Indeed reproducibility of a given set of data is of the order of a few parts in 10^5. Only when *independent* experiments are compared do discrepancies become clear and the major uncertainty is the true weight of polymer after degassing. Errors associated with each polymer appear quite random and we feel that the number of independent measurements is such that the standard deviation gives a realistic indication of the overall experimental accuracy.

Remarks have so far been confined to the liquid which is a thermodynamically well defined state. By contrast v_g depends on thermal history and was found less easy to reproduce. Differences of 3×10^{-4} cm^3/g noted for glasses which differ only in that the sample was molten between measurements are probably due to inefficient penetration of mercury into microvoids within the bulk of the sample. Changes in dilatometer geometry to give a larger surface to volume ratio would be useful. No systematic attempt was made to investigate the effect of thermal history on the glass (this is more conveniently carried out by calorimetry[6]) but a limited number of investigations were made on samples that had been cooled at 0.2°C/min or quenched into ice-water. For the latter v_g appeared to decrease with time even at room temperature but it was not clear if this was true annealing (60°–70°C below T_g) or merely slow penetration of mercury into the crazed polymer. Cooling at 0.2°C/min gave specific volumes that were some 10×10^{-4} cm^3/g higher than if cooled at 2.5°C/day. Quenching into ice gave a difference of $(20–25) \times 10^{-4}$ cm^3/g and this spread should encompass most literature values (details of thermal history are rarely given). *Table 3* clearly shows

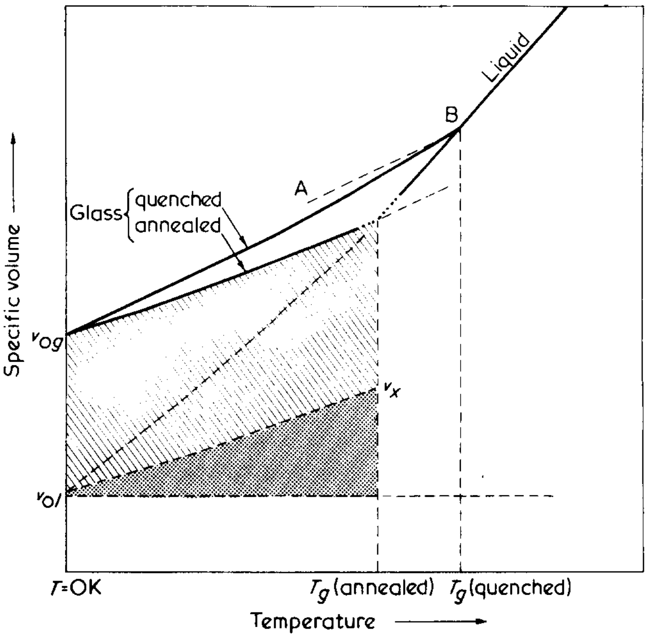

Figure 3 Schematic specific volume curves showing how T_g is defined. See text for discussion of free volumes.
$\alpha_z(T) = \partial \ln v_z / \partial T$ so that $v_{Tz}/v_{0z} = \exp \int_0^T \alpha_z(T) \mathrm{d}T$ where z = liquid or a given glass

much wider disparities in v_g and, since there is fair agreement for v_l, this is probably associated with incomplete coverage by the dilatometer fluid. This factor affects our results by, at most, 3×10^{-4} cm^3/g so that we believe there is an overall uncertainty of 8×10^{-4} cm^3/g in our values of v_g.

THE GLASS TEMPERATURE

Molecular weight relationships

The glass transition temperature, T_g, is defined as the point of intersection of specific volume curves for the 'equilibrium' glass and liquid[16] as shown in *Figure 3*, i.e. it is that value of T which satisfies the equation $v_g(T) = v_l(T)$. Since our interest is in the equilibrium glass we exclude all results in the vicinity (±15°C, dotted lines, *Figure 3*) of T_g since here rate effects are of major importance. Figures given in earlier sections allow the calculation of T_g in two different ways which should, of course, be equivalent in ideal conditions: 'observed' values, T_{go}, which are shown in *Table 2* and *Figure 4*, are the solutions of $v_g(T) = v_l(T)$ using the accompanying parameters for v_g and v_l; 'smoothed' values, T_{gs} have been calculated (full line, *Figure 4*) using equations (1) and (2) and the appropriate molecular weights. The simplest equation which relates T_g and M has the form:

$$T_g = T_{g\infty} - Z/M \qquad (3)$$

although this can only be an approximation since when M is very low the observed T_g is considerably higher than equation (3) predicts. Some idea of the range of validity of equation (3) can be obtained by fitting our data over various molecular weight ranges. Results are shown in *Figure 4*; using T_{go} there is virtually no difference when M is restricted (>10 000, $T_{g\infty} = 93.5$°C, $Z = 1.00 \times 10^5$, $\delta T = 1.5$°C) or all data are used (>2000, $T_{g\infty} = 93.5$°C, $Z = 1.02 \times 10^5$, $\delta T = 1.5$°C), δT is the standard deviation after curve fitting; T_{gs} must of necessity be a smooth function of M and in this case there is some virtue in restricting the range of application ($M > 10\,000$, $T_{g\infty} = 93.4$°C, $Z = 1.08 \times 10^5$, $\delta T = 0.05$°C; $M > 2000$, $T_{g\infty} = 93.2$°C, $Z = 1.00 \times 10^5$, $\delta T = 0.49$°C). The trivial standard deviation when $M > 10\,000$ shows that the simple equation (3) is a very good approximation above this value of M. However, since this conclusion is completely masked by experimental errors when T_{go} data are analysed we feel that for all practical purposes equation (3) is valid for $M > 2000$ with $T_{g\infty} = 93.4$°C and $Z = 1.02 \times 10^5$; we emphasize that these parameters refer to a glass formed by cooling the molten polymer through T_g at 2.5°C/day. The value of Z agrees well with previous estimates of 1×10^5 (dilatometry[8]) and 0.84×10^5 (d.t.a.[17]). The above data may be used to illustrate the curvature of the T_g–M^{-1} relationship at low M values. For $M = 580$ equation (3) with any of the $T_{g\infty}/Z$ parameters gives a T_g of about −80°C, whereas the solution of $v_g(T) = v_l(T)$ gives −48°C but even this is insufficient curvature to reflect the true value of about −30°C.

The sensitivity of the T_g–M^{-1} curve to small errors in T_g, especially at low M values, illustrates the problems encountered when seeking to identify molecular processes which may contribute distinct regimes to such curves[18]. Polystyrene is probably the polymer for which most reliable information is available but on the basis of existing data we are still reluctant to identify distinct regions as opposed to one smooth curve. In what may be an analogous case we have already seen how accurate measurements unambiguously demonstrate that the specific volume of liquid polystyrene is a quadratic function of temperature and this behaviour is merely approximated by two intersecting straight lines. The problem will only be resolved when T_g has been measured with an accuracy of a few tenths of a degree. Although this accuracy is, in principle, attainable using the thermodynamic definition of T_g given in this

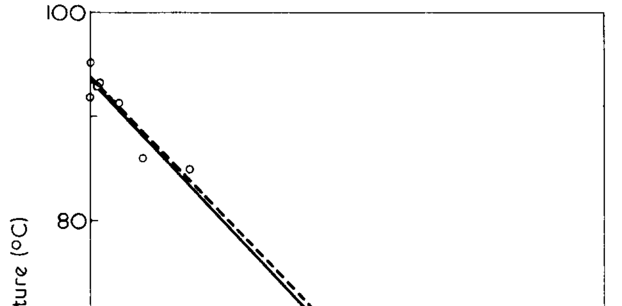

Figure 4 The glass temperature of anionic polystyrene as a function of M_n^{-1}. ○, Observed values (T_{go}) which give the linear fit shown by the broken line; ——, is the curve obtained (T_{gs}) using equations (1) and (2) to solve $v_g = v_l$. All glasses formed by cooling through T_g at 2.5°C/day

paper, in practice it is limited by the poorer reproducibility of v_g as opposed to v_l. We have already seen that when a sample was cycled l(liquid) → g(glass) → l → g, using the same $l \rightarrow g$ route in both cases, differences of up to 3×10^{-4} cm^3/g were found in corresponding v_g values but never in v_l. Assuming the two $v_g - T$ curves are parallel, a displacement of 3×10^{-4} cm^3/g implies a change of 1.5°C in T_g and this is the uncertainty associated with the present measurements.

Absolute values

Since the glass temperature of polystyrene is most frequently quoted (e.g. ref 19) as 100°C it might be thought that our $T_{g\infty} = 93.4$°C is exceptionally low but it is, in fact, a necessary consequence of the careful annealing our specimens have received in the vicinity of T_g. Although there are many schematic illustrations in the literature showing how T_g decreases with improved annealing of the glass, quantitative data for the effect of cooling rate appear nonexistent. Dilatometry does not allow a sufficiently wide range of practical cooling rates to investigate the effect and we have recently described a calorimetric technique[6] which allows a more efficient study of the problem. This shows that for polystyrene T_g decreases by 2.3°C for each decade decrease in cooling rate, a figure that is essentially independent of molecular weight when $M > 2000$. If we assume that the behaviour of the 'freeze-in' temperature parallels that of T_g the above figure compares very well with the value of 2.4°C/decade obtainable from the results of Goldbach and Rehage[5]. On this scale a transformation of T_g = 93.4° to 100°C would imply a change of cooling rate through T_g from 2.5°C/day to a few °C/min, a value which is reasonable for the 'natural' cooling of a few grams of polymer. 'Natural' cooling, as opposed to deliberate quenching or careful annealing, either of which would presumably be reported in the literature, will give a relatively narrow envelope of cooling rates and thus a fairly constant glass temperature so that for polymers with T_g well away from room temperature little scatter of T_g data would be expected. If, however, T_g is not far above ambient [e.g. poly(vinyl acetate)] storage will result in isothermal annealing, as studied by Kovacs[4], and T_g will vary with the age of the glass.

Free volume of polystyrene

The concept of 'free volume' (the total volume less some 'occupied' volume which may be specified in a number of ways) has been of immense value in explaining the temperature dependence of the mechanical properties of polymers in the glass transition region. Especially fruitful has been the concept of T_g as an iso-free volume state[8], i.e. the net of effect of the various physical and chemical structural parameters which affect T_g[20] is to change it until the 'universal' value is reached. Existing results now indicate that this may be too general a statement but a major problem is the lack of accurate data with which to test it. Suitable data for anionic polystyrene have been given in this paper and in this section we will consider how the free volume of this polymer is influenced by molecular weight and thermal treatment.

Quantities essential for any discussion of free volume are shown in *Figure 3*. At T_g thermal energy becomes sufficient to overcome 'lattice' forces and large scale molecular motion is possible. Holes, additional to those previously frozen in the glass, are formed and this is reflected in the relatively large value of α_l compared with α_g, which is due mainly to thermal vibration analogous to that in crystals. By this argument the free volume fraction, f, (oblique shading, *Figure 3*) is effectively fixed below T_g whereas above there is a steady increase with temperature, below T_g, $f = (v_{0g} - v_{0l})/v_{0g} = [v(T_g) - v_x]/v(T_g)$. This definition assumes that solid-like thermal expansion makes no contribution to f, an alternative definition (total shaded area, *Figure 3*), f', includes this so that $f'_{Tg} = [v(T_g) - v_{0l}]/v(T_g)$, and there is a discontinuity in $\partial f'/\partial T$ at T_g. The behaviour of f at T_g is usually examined by means of the equations $f = \Delta\alpha T_g$ and $f' = \alpha_l T_g$, where $\Delta\alpha = \alpha_l - \alpha_g$, but Simha and Weil[14] have shown that at best (α independent of temperature) these are approximations (higher order terms are neglected) and in general are of uncertain value since normally α is a function of temperature. In principle our equations (1) and (2) permit the calculation of all the relevant quantities shown in *Figure 4*. In the case of v_{0g} a fairly direct comparison with low temperature data[21] is possible and this is valuable in assessing the error due to our neglect in equation (1) of the change of shape of the $\alpha_g - T$ curve since $\alpha_g \rightarrow 0$ as $T \rightarrow 0$K[22]. Roe and Simha's measurements were made on quenched polystyrene and our extrapolated results parallel theirs but are a few percent lower; they are only 1–2% lower than Quach and Simha's[23] results on an annealed sample (cooled through T_g at 10°C/h). Low temperature results show singificant deviations from our extrapolated values of α_g only below ~60K, and in the region 0–60K the equation $\alpha_g = 2.4 \times 10^{-6} T$ approximates the experimental results. We can therefore calculate v_{0g} in two different ways: (a) directly via equation (1) and (b) via equation (1) to give v_{60} and then using $v_{60}/v_0 = \exp \int_0^{60} 2.4 \times 10^{-6} T \mathrm{d}T$. The results are for (a) v_{0g} = 0.9087 cm^3/g and for (b) 0.9118 cm^3/g so that the error in using equation (1) is only some 3×10^{-3} cm^3/g.

Extrapolated values of v_{0l} range from 0.7982 to 0.8005 cm^3/g for $M = \infty$ to 2050 and these figures give some confidence in the overall consistency of equation (2); the effects of chain ends are emphasized as T increases from 100° to 200°C so that the converse, a negligible contribution as $T \rightarrow 0$K, is intuitively reasonable. Again, over the same temperature range α_l increases by only 1.4[9] or 2.4% (equation 2) and this near invariance with temperature suggests that the major part of the admittedly lengthy extrapolation to v_{0l} can be charted with some confidence using equation (2). Many attempts have been made to better define the low temperature course of the $v_l - T$ curve to reduce the length of this extrapolation. These have generally used a theoretical equation of state plus experimental data on oligomers to extract corresponding states parameters which are in turn used to predict low temperature behaviour. However, we saw in an earlier section that equations of state normally give $\mathrm{d}\alpha/\mathrm{d}T$ which may be an order of magnitude greater than the experimental value. In the following discussion, therefore, we shall use v_{0g} and v_{0l} as obtained from equations (1) and (2). Errors will exist, due to our neglect of the decrease in α at the lowest temperatures, but being of the same sign they will tend to cancel in the calculation of free volume; errors will also be similar for different molecular weight so that *changes* in free volume with molecular weight, which are of most concern here, will be insensitive to extrapolation errors. *Table 4* shows the free volume and various fractions calculated according to the definitions given above. Over most of the molecular weight range the fractional free volume, however defined, is constant but there is a decrease at the lowest M values. Difficulties associated with any general quantitative treatment of polymers are clearly shown by the numerical value of $\Delta\alpha T_g$ – 0.123

Table 4 The free volume of polystyrene

M_n	$v_{og} - v_{ol}$ (cm^3/g)	$f_0 = \dfrac{v_{og} - v_{ol}}{v_{og}}$	$(\alpha_l - \alpha_g)T_g$	$f'_{T_g} = \dfrac{v(T_g) - v_{ol}}{v(T_g)}$	$\alpha_l T_g$
2050	0.1055	0.1164	0.1168	0.1671	0.1918
3660	0.1077	0.1187	0.1196	0.1712	0.1991
10400	0.1095	0.1206	0.1220	0.1748	0.2056
36000	0.1102	0.1213	0.1229	0.1762	0.2083
111000	0.1104	0.1215	0.1232	0.1766	0.2090
1990000	0.1105	0.1216	0.1233	0.1767	0.2094

in this work compared with the usually accepted 0.115[24,25]; if uncertainty still exists with regard to the basic physical properties of such a well investigated material as polystyrene there must be considerable doubt regarding data for most other polymers.

Although f remains nearly constant as T_g varies with M under constant glass-forming conditions, what is the position when the roles are reversed – constant M and variable glass forming conditions? By changing the latter we can, in principle, change T_g to any desired value. Let us consider an arbitrary increase of 10°C which implies a change of cooling rate from 2.5°C/day to 40°C/min[6], two limiting conditions in the volumetric behaviour can then be envizaged: either the new curve is parallel to that of the 2.5°C/day glass (AB *Figure 3*) or it extrapolates to a common v_{og}. In the former case there is an increase in free volume ($\Delta\alpha T_g$ increases from 0.123 to 0.126) whereas in the latter f_0 is unchanged. Clearly, therefore, T_g is *not* an iso-free volume state *if* α_g is characteristic of a given polymer, as is normally assumed, rather than restricted to a particular thermal treatment. It has already been indicated that the latter is correct since α_g(quench) > α_g(10°C/h) > (2.5°C/day) (quantities in parentheses refer to cooling conditions) but lacking full quantitative data for anything other than the 2.5°C/day glass we can only examine the behaviour of f as a function of annealing conditions in an indirect way. Assuming that v_{og} is common to all annealing treatments (i.e. at T_g the iso-free volume condition holds) and replacing $\alpha_g(T) = \partial \ln v_g/\partial T$ by some average value $\bar{\alpha}_g$, then $\ln(v_{T_g}/v_{og}) = \bar{\alpha}T$ and the problem is to see if the variation of $\bar{\alpha}_g$ with annealing conditions parallels the observed behaviour. For the 10°C/h glass $T_g = 98.0°C$ and v_g(98.0°C, 10°C/h) = 0.9721 cm^3/g (equation 2), v_g(98.0°C, 2.5°C/day) = 0.9706 cm^3/g (equation 1) so that taking v_{og} = 0.9807 cm^3/g, $\bar{\alpha}_g$(10°C/h)/$\bar{\alpha}_g$(2.5°C/day) = 1.023 which we consider to be good agreement with the observed difference (ref 23 and this work) of 1.8%. A similar comparison is not possible for the quenched sample of Roe and Simha[21] since the quench rate (and hence T_g) is not known but the observed ratio $\bar{\alpha}_g$(quench)/$\bar{\alpha}_g$(2.5°C/day) = 1.068 shows that α_g may vary widely for a given polymer.

In the above discussion we compare thermally polymerized and anionic polystyrene for which α is independent of preparative conditions (*Table 3*), the implicit, incorrect assumption that the specific volumes themselves are equal has a trivial effect on the conclusions since differences merely result in a vertical shift of all curves in *Figure 3* leaving, say, the difference $v_{og} - v_{ol}$ unchanged. The accord between observed and calculated values of α_g shows that for a given polymer the iso-free volume conditions hold for the wide range of glass temperatures obtainable by changing the *MW* or thermal history. It must be emphasized that this conclusion is restricted to an individual polymer and does not apply to the larger context of polymers in general for which the concept of an unique free volume fraction must be modified by the introduction of a geometric factor[26] to allow a meaningful comparison between polymers of very different structure.

CONCLUSIONS

Equations are given which allow the calculation of the specific volume of anionic polystyrene of $M = 2000 \rightarrow \infty$ at any temperature in the range –30° to 210°C. The specific volume of annealed polystyrene is a smooth (to $\pm 1 \times 10^{-4}$ cm^3/g) function of temperature in both the glassy and liquid states. Deviations from a linear T_g–M_n^{-1} relationship are less than the experimental error in the above molecular weight range but become large for lower molecular weights. The fractional free volume remains almost constant when T_g is changed by varying either the *MW* or annealing treatment.

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