PVT properties and equations of state of polystyrene: molecular weight dependence of the characteristic parameters in equation-of-state theories

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The pressure–volume–temperature (PVT) properties of styrene oligomers and polymers were studied experimentally in the liquid state. The data were fitted to various equations of state and the characteristic parameters in the equations of state, P^*, V^* and T^*, were obtained. A comparison was made of the performance of the various theories in fitting the data. The molecular weight dependence of the characteristic parameters was measured and the results indicated that the main variation arose from an increase in degrees of freedom per mer for lower molecular weights.

(Keywords: equation of state; dilatometry; polystyrene; molecular weight dependence)

INTRODUCTION

Equations of state provide us with useful descriptions of polymer liquid systems. Many equations of state have been suggested in order to describe the liquid state of polymers. Simple lattice theories are not adequate in describing the behaviour of polymer liquids. Various other theories have been developed which allow for the possibility of volume changes. Generally, they are derived by introducing a free volume term into the partition function. The most widely used equations of state for polymer liquids are the equation of state ascribed to Flory and coworkers[1,2], the lattice fluid theory of Sanchez and Lacombe (SL)[3], the Simha and Somcynsky equation of state (SS)[4] and the cell model (CM)[5].

Recently, a modified cell model equation of state (MCM) was proposed and was found to conform closely to experimental data[6]. These equations of state differ in the treatment of the free volume term and the energy term in the partition function. They provide us with valuable thermodynamic information in that the characteristic parameters, P^*, V^* and T^*, are related to various thermodynamic parameters of each polymer.

In this paper, we describe pressure–volume–temperature (PVT) measurements of polymers having different molecular weights. The molecular weight dependences of characteristic parameters in the equations of state are measured.

THEORY

There are numerous equations of state in the literature which are proposed to describe polymer liquids. In this paper, we mainly use two equations of state: the equation of state of Flory and coworkers and the cell model equation of state. The Flory equation has been most extensively applied. The cell model has been found to be a simple model which gives a much better fit to PVT data[5]. We examine the molecular weight dependence of the characteristic parameters in these two equations.

The equation of state of Flory and coworkers[1,2] is given by

$$\tilde{P}\tilde{V}/\tilde{T}=\tilde{V}^{1/3}/(\tilde{V}^{1/3}-1)-1/(\tilde{T}\tilde{V}) \qquad (1)$$

where $\tilde{P}$, $\tilde{V}$ and $\tilde{T}$ are the reduced variables defined as

$$\tilde{P}=P/P^*,\ \tilde{V}=V/V^*,\ \tilde{T}=T/T^* \qquad (2)$$

P, V and T being the actual pressure, volume, and temperature and P^*, V^* and T^* the characteristic parameters (hard-core reduction parameters) which must be found in order to characterize the system. P^* and T^* are given by

$$P^*=\varepsilon^*/V^*,\ T^*=\varepsilon^*/(ck) \qquad (3)$$

where ε^* is the mean intermolecular energy per contact pair, $3c$ is the number of external degrees of freedom per mer and k is the Boltzmann constant.

The cell model equation of state differs from the Flory model in that the latter uses a van der Waals potential to describe the attractive interaction between the mers in the system. The cell model employs a Lennard-Jones 6–12 potential to describe this interaction. The cell model equation of state is given by

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}}=\frac{1}{(1-\gamma^{1/3}\tilde{V}^{-1/3})}-\frac{2}{\tilde{T}}\left(\frac{A}{\tilde{V}^2}-\frac{B}{\tilde{V}^4}\right) \qquad (4)$$

where the definition of $\tilde{P}$, $\tilde{V}$ and $\tilde{T}$ is the same as the Flory model. The values of γ, A and B depend on the fraction of the cell volume filled at closest contact and factors taking into account interactions with other than the nearest neighbours, and these depend on the specific cell geometry used. For a hexagonal close-packed geometry, $\gamma=1/2^{1/2}$, $A=1.2045$ and $B=1.011$ (ref. 5). The

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goodness of fit is not found to be very sensitive to the geometry used, though the values of the reduced parameters will be different.

EXPERIMENTAL

Materials

The polymers used in this work were polystyrenes supplied by Polysciences and Scientific Polymer Products. These polystyrenes had a narrow molecular weight distribution. The characteristics are listed in *Table 1*. The polymers were pressed at 180°C, removed from the press and allowed to cool to room temperature. They were then broken into bubble-free pieces with dimensions of the order of 5 mm suitable for measurements.

PVT measurements

Densities of the polymers were measured at 25°C and atmospheric pressure using an autopycrometer (Micromeritics). The changes in density as a function of temperature and pressure were measured using a PVT apparatus, which has been fully described elsewhere[7]. For solid samples, it consists of a sample cell containing about 1–1.5 g of sample and mercury as a confining fluid. A flexible bellows closes off one end of the cell. The movement of the bellows on changing temperature or pressure is used to calculate the volume change of the sample cell. In the isothermal mode, volume readings are obtained at fixed pressure intervals (usually 10 MPa) at a constant temperature. After measurements along an isotherm, the temperature is increased by 8–10°C and the process is repeated. The absolute accuracy of the device is $10^{-3}-2\times10^{-3}\,\mathrm{cm^3\,g^{-1}}$; however, volume changes as small as 10^{-4}–$2\times10^{-4}\,\mathrm{cm^3\,g^{-1}}$ can be resolved. A version of this PVT apparatus is available as a complete instrument from Gnomix Research, Boulder, CO, USA.

RESULTS AND DISCUSSION

Figure 1 shows typical PVT data taken for polystyrene (PS114K) in the form of isobars at intervals of 40 MPa (only some of the data is shown for clarity). Data were obtained for each of the polystyrene samples and all were qualitatively similar to those shown in the figure. The appearance of these isobars is typical of a glassy material undergoing a transition to the melt state as the temperature increases. At zero pressure there is a break in the volume *versus* temperature curve near 100°C, marking the zero-pressure glass transition temperature. Line A is an isotherm through this point. All data lying to the left of this line belong to the PVT relationship of the particular glass that was loaded into the PVT apparatus. Line B in *Figure 1* is defined by the intersection of the quasi-equilibrium PVT data to the left of line A with the equilibrium melt data. By analogy with the operational definition of the zero-pressure glass transition temperature, one can interpret this line as marking the pressure-dependent glass transition of the original glass. No attempt was made to control exactly the nature of the glass loaded in the cell. The theories we use here are unsuitable for describing the properties of a glass, though the theory of Simha and Somcynsky has been used in this way[4]. The melt data does not depend on the glass used.

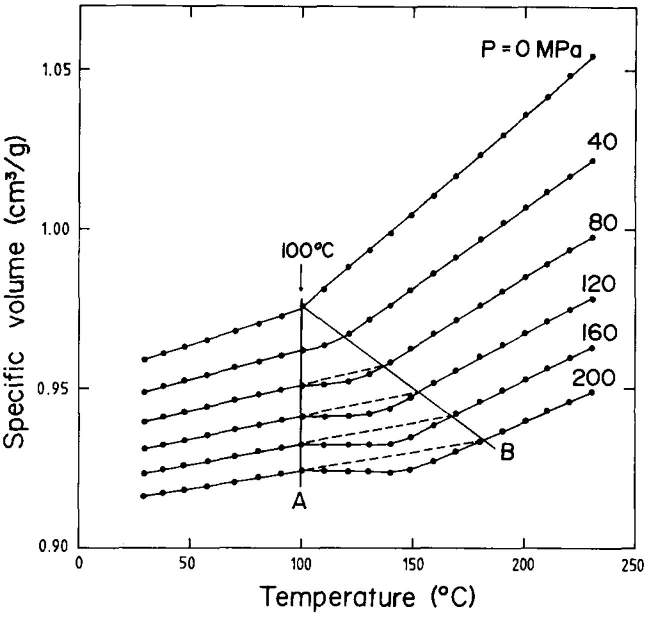

Figure 1 Isobars at intervals of 40 MPa for polystyrene (PS114K). Line A is an isotherm through the zero-pressure glass transition temperature (100°C). Line B indicates the intersection of the data for the glass to the left of line A with the data of the melt

Table 1 Material characteristics

Code	M_w[a]	M_w/M_n[a]	Density (±0.003) (g cm^{-3}) (25°C)
PS0.9K	910	1.16	1.026
PS2K	2 200	1.195	1.040
PS4K	3 800	1.06	1.039
PS9K	9 000	1.06	1.035
PS17.5K	17 500	1.03	1.039
PS34.5K	34 500	1.06	1.039
PS110K	110 000	1.06	1.045
PS114K	114 200	1.04	1.045
PS612K	612 000	1.06	1.040
PS929K	929 000	1.14	1.043
PS2M	2 100 000	<1.30	1.043

[a] M_w is the weight average and M_n the number average molecular weight in g mol^{-1}

The data for the liquid state were taken to the right of line B (the region of higher temperature below the thermal degradation temperature).

For each of the polymers we fitted the melt PVT data to the equations of state. We performed a nonlinear least squares fit of each equation by minimizing the quantity

$$S^2=\textstyle\sum_i(P_{i,\mathrm{data}}-P_{i,\mathrm{fit}})^2/(N-3) \qquad (5)$$

where N is the number of data points; P_{data} is the measured pressure at a given value of (V, T) for the system and P_{fit} is the value of the pressure predicted by the relevant equation of state. We feel that this procedure provides a fair criterion for comparing the goodness of fit of various equations of state.

Table 2 shows the example of the results of the fitting procedure when applied to polystyrene (PS114K). The region of data is above the T_g to 230°C and from 10 MPa to 200 MPa at intervals of 10 MPa. The cell model equation provides a moderately good fit. This tendency is the same for other polystyrene specimens. It should be pointed out that the poor fit of the Flory equation means that the values of the characteristic parameters in this

Table 2 Characteristic parameters and values of goodness of fit parameter S^2 for PS114K[a]

	P^*	V^*_{sp}	T^*	S^2
Flory	461.03	0.82193	7860.28	8.1400
CM	622.89	0.90778	4924.71	1.7927

[a] T_g to 230°C, 10–200 MPa

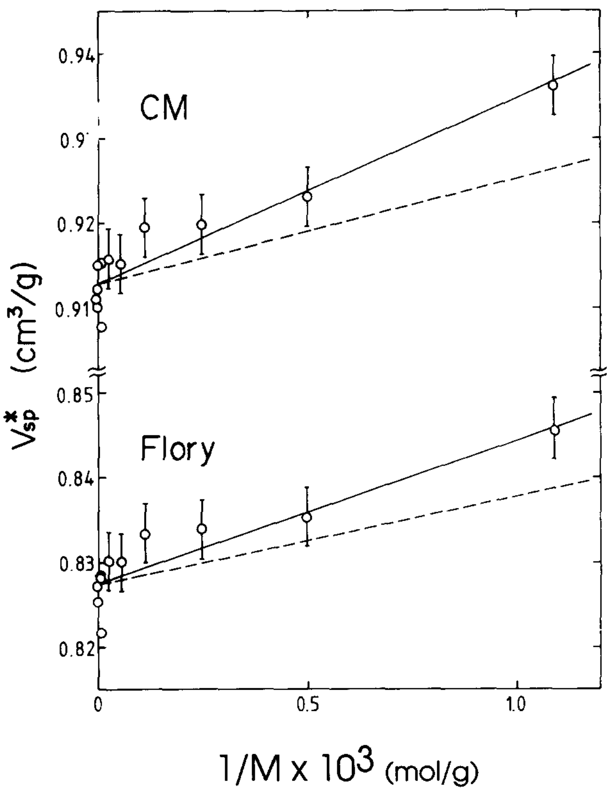

Figure 2 Molecular weight dependence of V^*_{sp}. ---, Calculated from equations (7a) and (7b); ——, least squares fits to the data

case will depend very much on the temperature and pressure range of the data.

When we consider the molecular weight dependence of the characteristic parameters, the contribution from end groups has to be considered. Generally, if the contribution of an end-group can be distinguished from that of the main chain, it is effective on the basis of the volume fraction of end groups. In this case, the molecular weight dependence of the characteristic parameters is then given by

$$X = X_{\infty} + \mathrm{const.}/M \qquad (6)$$

where X is the particular characteristic parameter and M is the number average molecular weight of the polymer. The following plots are based on equation (6). The errors in these plots are estimated from repeated measurements at high molecular weight.

The characteristic volume (V^*_{sp}, hard-core specific volume)

Figure 2 shows the plot of V^*_{sp} *versus* $1/M$. Obviously, V^*_{sp} depends on molecular weight and decreases as the molecular weight increases. We can consider a contribution from the end groups. The end group of polystyrene is (C_4H_9) on one side and –H on the other side. We used the characteristic parameters of polyethylene[5] shown in *Table 3* as an approximation to the end group. Using polyethylene data is not expected to be an exact solution but should give an order-of-magnitude estimate of the effect the end groups should have.

Considering the volume fraction of the end group, the molecular weight dependence of V^*_{sp} of polystyrene would be approximated by

$$\text{Flory:} \quad V^*_{sp} = V^*_{sp\infty} + 10.5/M \qquad (7a)$$

$$\text{CM:} \quad V^*_{sp} = V^*_{sp\infty} + 12.3/M \qquad (7b)$$

These are shown by the broken lines in *Figure 2* and are close to the experimental results. Low molecular weight samples, however, deviate from the line.

The end-group effect, thus calculated, accounts for most of the molecular weight dependence of V^*_{sp}.

The characteristic pressure (P^*)

Figure 3 shows a plot of P^* *versus* $1/M$. As indicated by equation (3), P^* is related to ε^*. It may not be a good approximation to consider values as the sum of those of end and middle groups, since there may exist a self-interaction between end and middle groups. Within experimental error, however, one cannot predict any molecular weight dependence of P^*. This is because the error in P^* is large (about ±15 MPa). The contribution of the end group calculated as above is < 10 MPa for the lowest molecular weight, PS0.9K, using both models. Thus, the molecular weight dependence of P^* is not resolved due to the error in determining P^*.

Table 3 Characteristic parameters of polyethylene[5]

	P^* (MPa)	V^*_{sp} (cm^3 g^{-1})	T^* (K)
Flory	516.8	1.0076	6821.6
CM	587.6	1.1265	4340.9

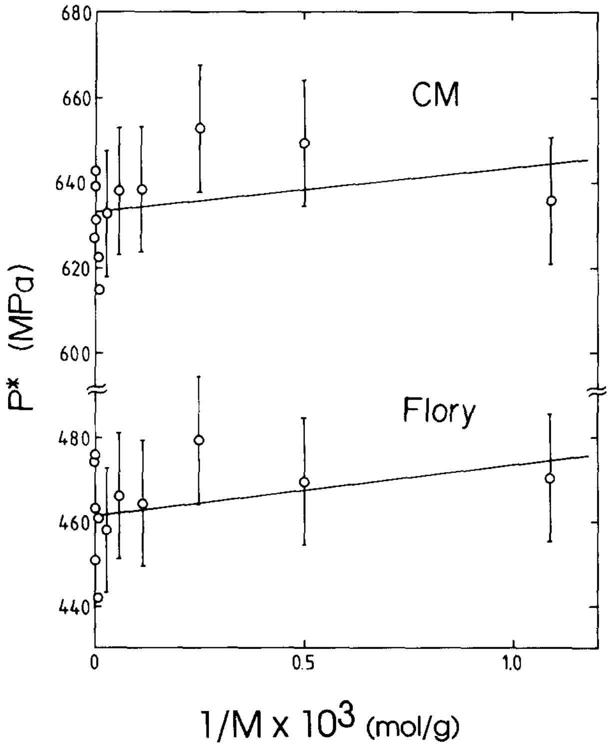

Figure 3 Molecular weight dependence of P^*. ——, Least squares fits to the data

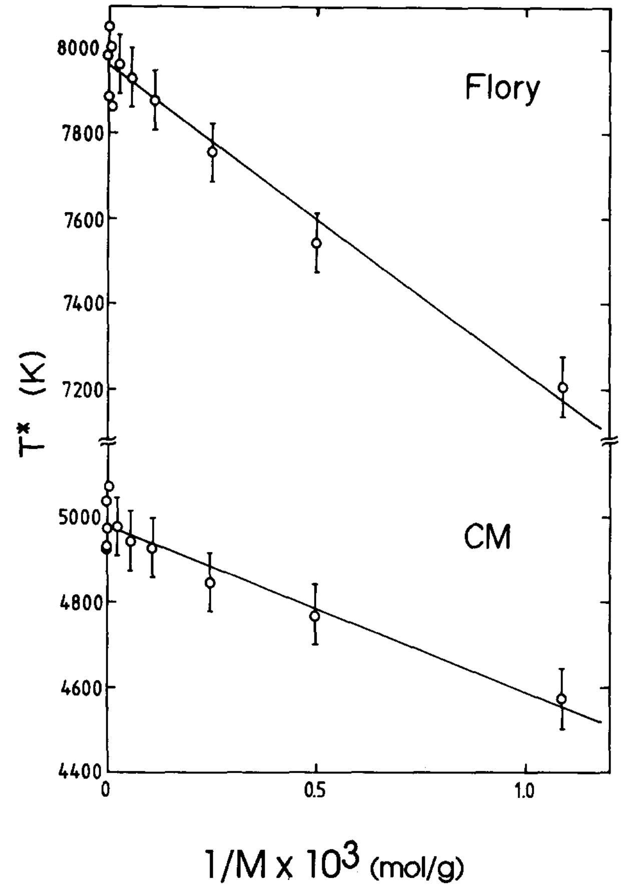

Figure 4 Molecular weight dependence of T^*. ——, Least squares fits to the data

The characteristic temperature (T^*)

Figure 4 shows the plots of T^* *versus* $1/M$. T^* clearly depends on the molecular weight. When considering the volume fraction of end groups, however, the contribution is <30 K for PS0.9K using the Flory model and is much less than the molecular weight dependence of T^* found experimentally. T^* is given by

$$T^* = P^*V^*/(ck) \tag{8}$$

The molecular weight dependence is much larger than that of P^* and V^*. Accordingly, it is considered that the molecular weight dependence of c is large.

The external degrees of freedom (c)

Figure 5 shows the plots of c/Mo *versus* $1/M$. The ratio c/Mo is given by

$$\frac{c}{Mo} = \frac{P^*V^*_{\mathrm{sp}}}{\mathrm{RT}^*} \tag{9}$$

where R is the gas constant and Mo is the molecular weight per segment (not necessarily equivalent to a monomer).

Let us consider the total number of degrees of freedom of the chain to be $3c_t$. If the universal assignment $\lim_{s\to\infty} 3c_t/s = 1$ is adopted[8], the following equation applies:

$$3c_t = s + K \tag{10}$$

where s is the number of segments per chain and K is a constant. Then, c/Mo is given by

$$\frac{c}{Mo} = \frac{1}{3Mo} + \frac{K}{M} \tag{11}$$

Generally, K is not zero, even if there is no difference between the end groups and the rest of the chain. Jain and Simha adopted $K = 3$ for oligomers[9]. If the end group is different from the rest of the chain, then K will have a different value. *Table 4* shows the values of K from experimental data. Mo can be obtained from the intercept in the plot of c/Mo *versus* $1/M$. The resulting values are shown in *Table 4*. This indicates that the size of a segment differs with the model. The cell model treats the segment as small in comparison with the Flory model. The ratio of Mo to the repeat unit molecular weight is also shown.

The glass transition temperature (T_g)

Figure 6 shows the molecular weight dependence of T_g at zero pressure. T_g is expected to be only very weakly dependent on the nature of the glass loaded into the machine and all glasses were produced in the same way. The straight line is given by

$$T_g = 373 - 7.0 \times 10^4/M \tag{12}$$

The coefficient of $1/M$ is slightly smaller than the result of Fox and Flory[10]. The molecular weight dependence of T_g is similar to that of T^*. Dibenedetto assumed that

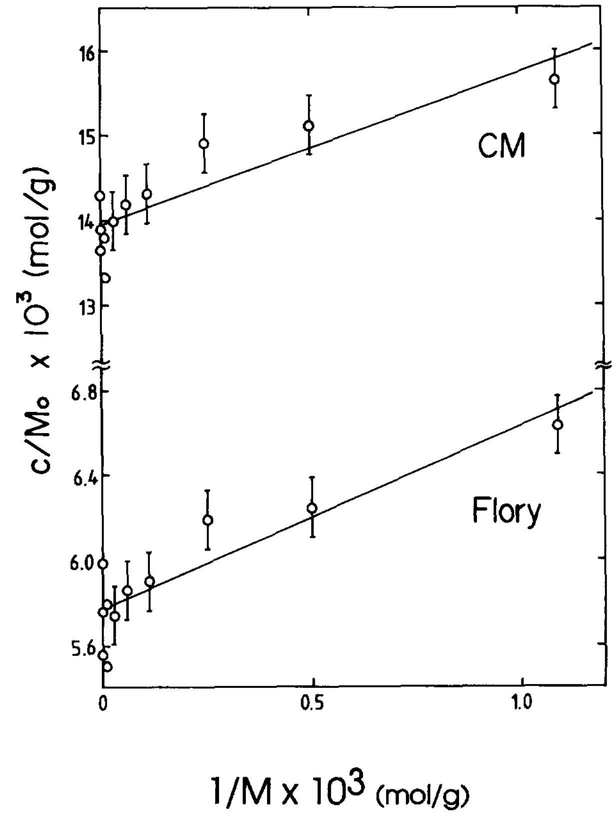

Figure 5 Molecular weight dependence of c/Mo. ——, Least squares fits to the data

Table 4 Values of K and Mo from equation (11)

	K	Mo	$M_{\mathrm{rep}}{}^a/Mo$
Flory	0.86	57.6	1.81
CM	1.78	23.9	4.36

^{a} M_{rep} is the molecular weight of the repeat unit (104.2 g mol^{-1})

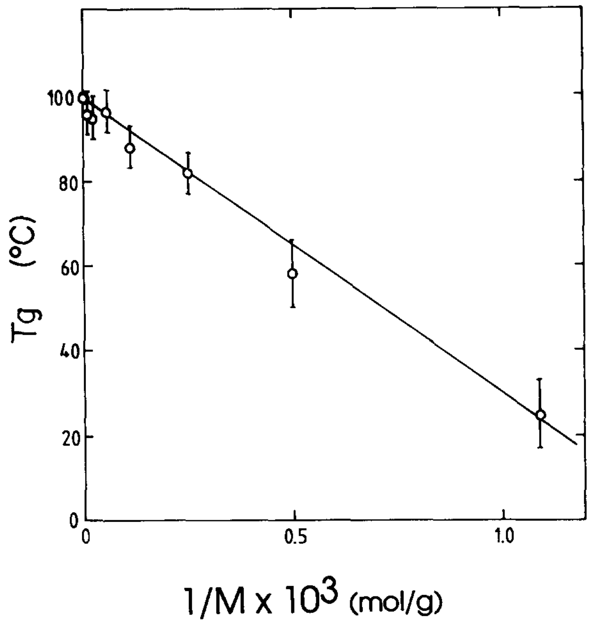

Figure 6 Molecular weight dependence of glass transition temperature T_g. ——, Least squares fit to the data

there is a single universal value for the reduced glass transition temperature (i.e. $T_g/T^* = \text{const.}$) at zero pressure[11]. He then predicted the effect of the molecular weight on the glass transition temperature by using the approach of Flory[1] and Prigogine[12]. His assumption is given by

$$\frac{T^*_{g_x}}{T^*_{g_\infty}} = \frac{T_{g_x}}{T_{g_\infty}} \tag{13}$$

where X is the number of segments. Our experimental data do not agree with equation (13).

At zero or atmospheric pressure ($\tilde{P} = 0$), the Flory equation of state (equation (1)) is expressed as

$$\tilde{T} = (\tilde{V}^{1/3} - 1)/\tilde{V}^{4/3} \tag{14}$$

T_g is given by

$$T_g = T^* \frac{\tilde{V}_{T_g}^{1/3} - 1}{\tilde{V}_{T_g}^{4/3}} \tag{15}$$

where $\tilde{V}_{T_g}$ is the reduced volume at T_g. If $\tilde{V}_{T_g}$ does not depend on the molecular weight and is constant, the assumption of equation (13) is correct. However, it is not constant and equation (13) is not generally satisfied. $\tilde{V}_{T_g}$ tends to increase with increasing molecular weight from our data. The molecular weight dependence of $\tilde{V}_{T_g}$ has not, however, been predicted by theory.

CONCLUSION

We have investigated the molecular weight dependence of the characteristic parameters in two equations of state for polystyrene using PVT measurements. The molecular weight dependence of V^*_{sp} can be interpreted by considering the volume fraction of the end groups. The variation of P^* is less than experimental error and cannot be discriminated. That of T^* is large and results from a large molecular weight dependence of the external degrees of freedom c. Moreover, it is indicated that T_g is determined by both T^* and $\tilde{V}_{T_g}$.

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