

Viscosity of Polystyrene near the Glass Transition

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Synopsis

A quantitative explanation is given for the apparent viscosity increase with increasing capillary shear rate for polystyrene at temperatures approaching the glass transition, T_g . Possible shifts in T_g as a function of the parameters shear rate, frequency, and pressure are interrelated to viscosity changes. Experimentally, the Instron capillary rheometer and the Weissenberg rheogoniometer provided a means for uncoupling the variables for individual consideration. Calculated and experimental data for the apparent viscosity as a function of the given parameters are presented and discussed. The explanation of the apparent viscosity increase in capillary flow can be quantitatively explained through the pressure dependence of T_g . Brief mention is made of the pressure effects on the Bagley and Rabinowitsch corrections normally made in capillary measurements.

INTRODUCTION

Anomalous viscosity increases with increasing shear have been reported for both amorphous and crystalline polymer systems.^{1,2} This behavior has been reasonably explained for crystalline polymers. No quantitative interpretation has been given, however, for the viscosity increase of amorphous polymers other than an exponential dependence of viscosity on pressure.^{3,4} This study considers possible explanations for this anomalous behavior by measurements made on high and low molecular weight polystyrenes of narrow distribution.

The viscosity increase, as presented by Ballman¹ for a high molecular weight polystyrene, was most noticeable at temperatures approaching T_g , down to 136°C, and disappeared at high temperatures, around 200°C. The glass transition appeared, therefore, to be a region of prime importance. Its potential shift with the interdependent variables pressure, frequency, and shear rate was considered as a possible cause for the viscosity increase. This explanation can involve representing a change in T_g as a change in viscosity.

The parameters pressure, shear rate, and frequency were separated by the use of different viscometers, and temperatures of measurement for both the low and high molecular weight polystyrenes approached their respective glass transition regions. Experimental and calculated data of viscosity as a function of frequency, shear rate and pressure are discussed.

Shifts of T_g with pressure were converted to a viscosity change using available P - V - T data and the well-known WLF and Tammann-Hesse equations. The calculated change in viscosity was combined with the zero shear viscosity values for the polystyrenes with a molecular weight below M_c , the critical entanglement molecular weight. For polystyrene tested with a molecular weight above M_c , a suitable power law expression for shear thinning was combined with the pressure effect. This provided a direct comparison between calculated and experimental data.

EXPERIMENTAL

Samples

Narrow distribution samples of low (19.6K, 20.4K) and high (670K) molecular weight polystyrene were obtained from Pressure Chemicals. The low molecular weight polystyrenes had a $M_w/M_n \leq 1.06$ and the 670K sample had a $M_w/M_n \leq 1.10$. Sufficient material was available to limit the use of each aliquot to one pass, thus minimizing the effects of degradation which could occur in successive passes of the same sample.

Cone-Plate Viscometer

The Weissenberg rheogoniometer (Model No. 17) provided the means to separate the variables shear rate and frequency from pressure. Dynamic measurements on the 19.6K sample were made with a cone and plate diameter of 2.54 cm and a 4° cone angle. A cone and plate diameter of 5.03 cm with a 2° cone angle was used for steady-state viscosity measurements of the 20.4K and 670K samples. Steady-state measurements were made in both directions of rotation and data taken only within the region where heat generation was not significant. At successively higher shear rates, a sufficient time was allotted between measurements to allow the system to thermally equilibrate. Nitrogen gas was used to thermostat and to minimize degradation which might occur at higher temperatures and shear rates. The samples were inserted in the instrument in a way which virtually eliminated air voids.

Capillary Viscometer

The effects of pressure were studied using an Instron capillary rheometer with a main barrel diameter of 0.375 in. Several capillaries were used. These include, in units of inches, 0.060 diameter and 0.257 length ($L/D \approx 4/1$), 0.020 diameter and 1.01 length ($L/D \approx 50/1$) and 0.030 diameter and 3.00 length ($L/D \approx 100$). All capillaries had an entrance angle of 90° . Data points were rechecked on successive days and the reproducibility was periodically verified. Possible heating effects at higher shear rates were checked by reducing the shear rate and comparing the stress to that originally obtained without shear heating, by waiting a sufficient time between measurements and by observing any decrease in load with time. The

total stress capacity of the instrument was usually reached, especially at the lower temperature, long before shear heating became appreciable.

A number of possible capillary corrections were considered. The kinetic energy correction was negligible for the conditions used here. Both the elastic energy or Bagley correction⁵ and the Rabinowitsch⁶ or nonparabolic flow correction were considered. The Rabinowitsch correction is not required for Newtonian flow, and, for simple power law non-Newtonian behavior, is reasonably straightforward to apply as is the Bagley correction in the absence of pressure effects. However, as will be seen, deviations from Newtonian and power law behavior occur under the influence of pressure. It thus becomes impossible to justify either of these corrections for pressure-dependent viscosities. Under these conditions shear stress is observed to increase markedly with little increase in shear rate to a level which rapidly exceeds the load capacity of the capillary instrument. This effect becomes ever more noticeable as the test temperature is decreased. The Bagley correction, based on a linear extrapolation of pressure versus L/D , becomes nonlinear at sufficiently high L/D ratios. The exact L/D ratio at which it becomes nonlinear is apparently a function of the temperature and shear rate. The lower the temperature and higher the shear rate, the lower the L/D at which the nonlinearity appears. Additional comments on the application of capillary corrections will be mentioned in a later section.

RESULTS AND DISCUSSION

An increase in viscosity for the amorphous polymer polystyrene with increasing shear rate has been reported previously.^{1,2} It has been independently suggested that this increase is exponentially dependent on pressure.³ It is of interest to examine this phenomenon more closely and to ascribe, if possible, a quantitative explanation to the anomalous viscosity increase with increasing shear. From Ballman's data¹ it is apparent that the viscosity increase becomes ever more noticeable as the temperature is decreased toward the glass transition temperature, T_g . At T_g the viscosity is known to be $\geq 10^{10}$ poises, a range quite inaccessible by steady-flow measurements made with instruments such as the Instron rheometer and Weissenberg rheogoniometer. What is interesting to note, however, is that both the previous data and some of these new results show a sharp increase in viscosity with increasing shear rate at 30°C and more above the nominal glass transition which is near 100°C for the high molecular weight polystyrene. By extrapolation to yet higher shear rates, it is possible to visualize viscosities corresponding to the glass transition temperature. By restricting molecular motions of an amorphous polymer to those associated with the glass transition region, one can effectively cause a marked shift in the glass transition temperature. It is this possible shift in T_g and its relationship to viscosity which is discussed in terms of the measureable parameters shear rate, frequency, and pressure.

Assuming the relationship of T_g with a given parameter to be known, the WLF equation may be used to calculate the anticipated viscosity change.

Consider the WLF equation where C_1 and C_2 have been tabulated for different polymers including polystyrene:⁶

$$\log \eta/\eta_0 = \frac{-C_1 (T - T_g)}{C_2 + T - T_g} \quad (1)$$

Knowing η_0 and holding T , the test temperature, constant, a change in η can be found by inserting the various values of T_g calculated from the response to a given parameter. This change in viscosity can then be combined with η_0 for a polystyrene exhibiting Newtonian flow or with a power law expression for the non-Newtonian (high molecular weight) polystyrenes. If there is no change in T_g with a given parameter, no viscosity change will be predicted.

The first consideration will be to see how a change in shear rate (at constant pressure) or a change in frequency might affect a change in viscosity through a shift in the glass transition temperature. Lewis has collected data on the dynamic glass transition measured at several frequencies for many polymers.⁷ Rearranging his semiempirical equation gives the following equation for the frequency dependent T_g , called T_d :

$$T_d = \Delta H_a / [-(\log \nu_d/\nu_c) 4.57 + T_c \Delta H_a] \quad (2)$$

where ΔH_a = activation energy for the glass transition, ν_d = frequency of measurement, T_d = dynamic glass transition, and ν_c, T_c = constants for a given polymer. $\Delta H_a, \nu_c$, and T_c were evaluated for polystyrene using data given by Lewis. A considerable shift in T_d of 30°C and more was predicted for an experimentally accessible range of frequencies. The same correlations were used for steady shear measurement comparisons with Weissenberg data by using a factor of 2π . The justification for this rests on past favorable comparisons of dynamic and steady-state data in the onset region for non-Newtonian flow and the dimensional consistency of frequency and shear rate. This conversion is made with the recognition of possible fallibility due to different mechanisms occurring in dynamic and steady-state deformations.

Figure 1 compares experimental data from the Weissenberg viscometer with viscosities calculated by using the combined Lewis and WLF equations as described above. An increase in shear rate was converted to a shift in T_g using the Lewis equation. This shift was used in the WLF equation to calculate the increase in viscosity. The calculated viscosity increase was combined with η_0 , superimposing the curves at the lowest shear rate measured. The results in Figure 1 clearly indicate that the calculated curves diverge from the experimental points, predicting an increase at high shear where in fact none occurs in the data. Similar results were obtained in comparisons of dynamic viscosity measurements on the high and low molecular weight polystyrenes and for steady-state measurements of the high molecular weight polystyrene.

The reason why an increase in viscosity with frequency is predicted where none occurs experimentally is not entirely clear in view of the large change in

T_d with frequency presented by Lewis.⁷ The change in T_g with frequency likely occurs but this is not reflected in a viscosity increase. The discrepancy in the steady-state measurements might also be in the inappropriate application of dynamic glass transition data to the steady-state flow. It can be clearly concluded from the Weissenberg data that no viscosity increase occurs in dynamic or steady-state data for high or low molecular weight polystyrenes, at least in the temperature and shear ranges studied.

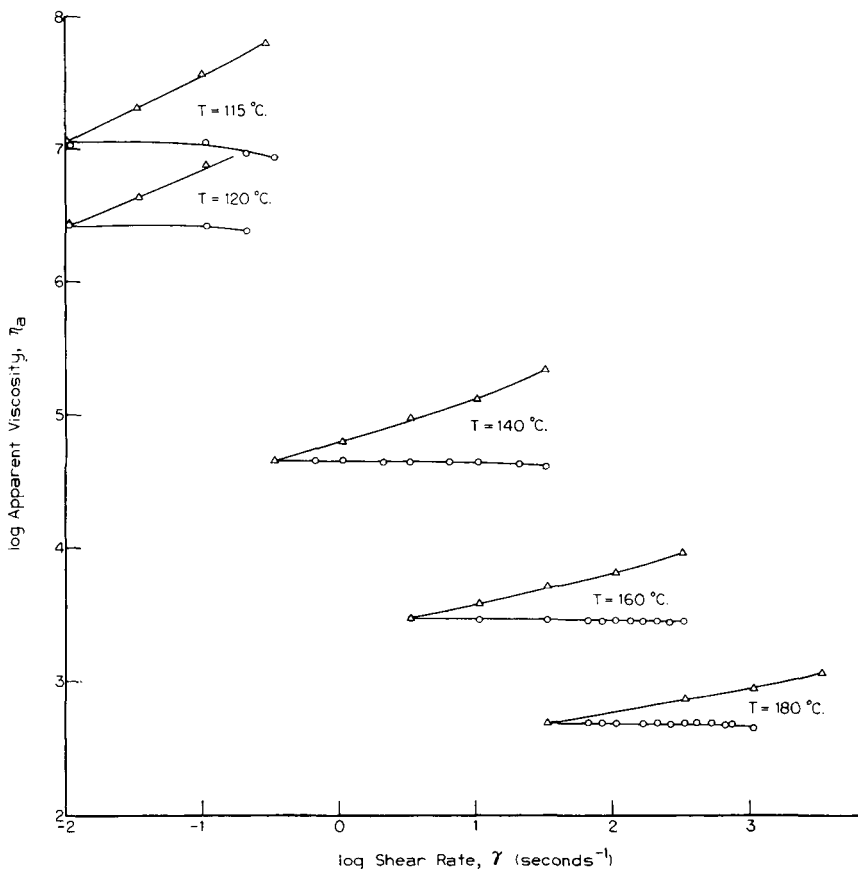


Fig. 1. Comparison of experimental data from Weissenberg rheogoniometer and calculated apparent viscosities for narrow-distribution low molecular weight polystyrene ($M_w = 20,400$; $M_w/M_n \leq 1.06$): (O) experimental (Weissenberg visc.); (Δ) calculated (Lewis plus WLF equations).

Pressure effects on viscosity were independently studied in this work using an Instron capillary rheometer. Varying the shear rates and temperature gives an indication of how the variable pressure affects the viscosity, in that increasing the shear rate is effectively the same as increasing the pressure. It is possible to use an exponential pressure dependence of viscosity and with experimental data to calculate the exponential and preexponential

constants.^{3,4} However, a more quantitative approach to the prediction of viscosity under pressure in a capillary has been considered here.

In the glass transition region molecular motions are limited to those involving a distribution of short-chain segments.⁸ Any external influence which reduces the motion of polymer subsegments to those corresponding to the glassy state will effectively shift the glass transition. Pressure is an external influence which can operate by reducing free volume and long-range coordinated molecular motions. With a shift in the glass transition to a higher temperature, the observation of higher viscosities can be expected. It appears of interest, then, to consider how pressure affects the free volume and T_g , and how these features influence the apparent viscosity.

Considerable P - V - T data is available for polystyrene^{9,10} from which the shift in the glass transition can be evaluated using, for example, the Tait¹¹⁻¹³ equation

$$V_0 - V = V_0 \ln [1 + P/B] \quad (3)$$

where V = volume at pressure P , V_0 = volume at zero pressure, and B = (bars) temperature-dependent parameter (constant under isothermal conditions).

The Tait equation originally was used in studying the P - V relationships of sea water.¹¹ It was subsequently found to be applicable to polystyrene.^{12,13} Differentiating the Tait equation with respect to pressure and temperature results in expressions for the compressibility and coefficient of expansion, respectively, which were used by Gee and Miller in their T_g versus pressure calculations.^{12,14} Gee evaluated the Tait equation constants and used it to calculate the volume which he then subtracted from the measured volume. Plotting this difference (at several temperatures) as a function of pressure and extrapolating to zero difference in volume, Gee obtained a linear relationship between pressure and the glass transition as given by the following equation:

$$T_g = T_{g0} + 0.028P \text{ (bars)}. \quad (4)$$

The data of Gee is apparently for a low molecular weight polystyrene as indicated by his value of T_{g0} at atmospheric pressure of 90°C. By changing the value of T_{g0} to 100°C, this same relationship was used here for flow data on high molecular weight polystyrene.

Miller approached the pressure dependence of T_g somewhat differently but with essentially the same result.¹⁴ Considering the viscosity to depend P , V , and T and assuming T_g to be an isoviscous state, he arrived at the following relationship, where α_i (thermal expansion coefficient) and β_i (compressibility coefficient) are calculated using Gee's expressions derived from the Tait equation, where v_g is the specific volume of the glass.

$$\frac{dT_g}{dP} = \frac{\beta_i}{(1/v_g)(dv_g/dT) - \alpha_i} \quad (5)$$

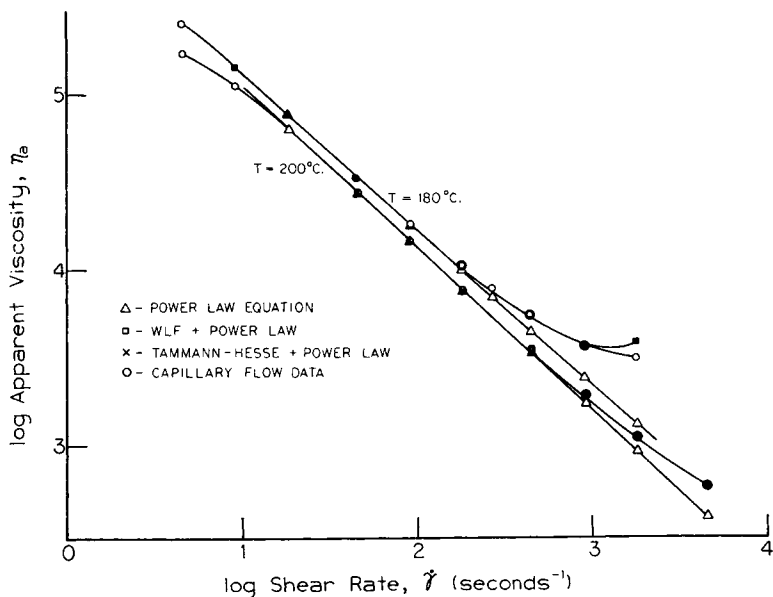


Fig. 2. Capillary flow data compared with calculated apparent viscosities for narrow-distribution high molecular weight polystyrene at 180° and 200°C ($M_w = 670,000$; $M_w/M_n \leq 1.10$).

Miller's expression, eq. (5), can be used to calculate the desired T_g -pressure relationship if sufficient P - V - T data is available. What remains to be done is to combine this shift in T_g with a suitable expression for calculation of possible viscosity changes with pressure.

The WLF equation was used previously to calculate the viscosity increase and is also applied here. A second means of determining the exponential dependence of viscosity on pressure was also considered based on correlations made by Miller.¹⁴ Using Williams' "free volume" expression¹⁵ of the melt viscosity for a series of polystyrene fractions (measured by Fox and Flory⁹), Miller correlated the free volume parameters with those given in the Tammann-Hesse¹⁶ equation;

$$\log \eta = \log A + B/(T - T_0). \quad (6)$$

The parameters A , B , and T_0 were then evaluated by Miller using the available data for the polystyrenes. By assuming that a change in T_0 is equivalent to a change in T_g , as Miller did, a second means of calculating the pressure dependence of viscosity is available.

Figure 2 is a comparison, for high molecular weight polystyrene, of results obtained experimentally and viscosities calculated independently using the WLF and the Tammann-Hesse equations. The viscosity increase was combined with a power law expression to produce the calculated results. At 200°C, all points superimpose with very little deviation from power law behavior. At 180°C, appreciable power law deviation occurs and signifi-

cantly is predicted reasonably well by either the WLF or the Tammann-Hesse equations. As the test temperature is lowered, the increase in capillary pressure necessary to obtain a given shear rate increases the viscosity, apparently through a shift in the glass transition temperature. This effect becomes ever larger as the test temperature is decreased, as shown in Figure 3. It may be noted that the viscosity increase observed in pressure capillary is also predicted quite well by either of the two methods of calculation at both 165° and 150°C. The pressure required for flow at 150°C in the shear rate range of 10 sec⁻¹, according to the data of Gee,¹¹ is equivalent to shifting the glass transition 45° or more. Assuming the glass

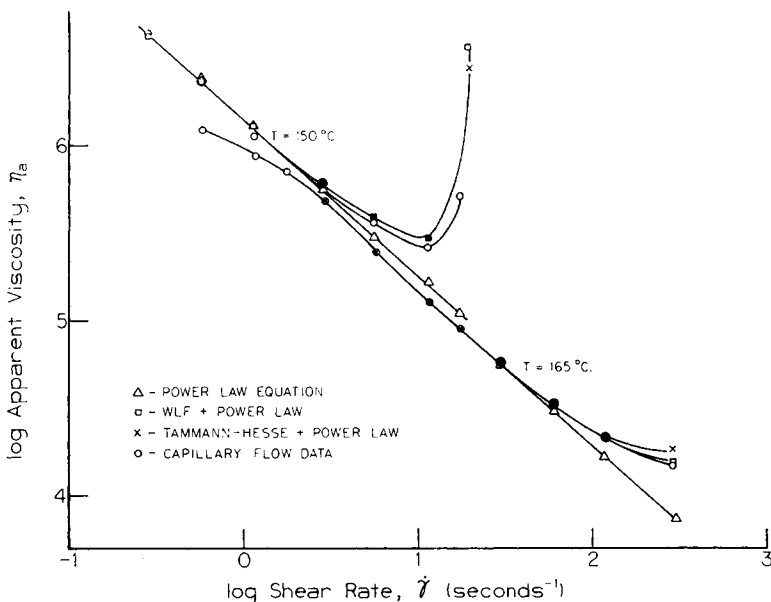


Fig. 3. Capillary flow data compared with calculated apparent viscosities for narrow-distribution high molecular weight polystyrene at 150° and 165°C ($M_w = 670,000$; $M_w/M_n \leq 1.10$).

transition to be approximately 100°C for this polystyrene at atmospheric pressure, a glass transition in the region of 145°C is then predicted at the higher pressures. This would certainly seem to account, then, for the very rapid rise in viscosity with shear rate at 150°C.

Viscosity data, comparable to that in Figure 3, is presented for a low molecular weight polystyrene in Figure 4. Recall that for essentially Newtonian behavior the calculated viscosity change with pressure is simply added to the zero shear viscosity. At 180°C, the behavior is Newtonian as predicted by calculation and verified experimentally by both the Weissenberg and Instron capillary instruments. As the test temperature is decreased, the pressure effect becomes more noticeable and is predicted well at all test temperatures which were performed down to 120°C. The behavior

in the Weissenberg viscometer is Newtonian at all temperatures and shear rates studied indicating that in the absence of increasing pressure no viscosity increase or decrease occurs. The pressure required in the capillary at the highest shear rates, both at 120° and 140°C, was sufficient to cause an apparent shift in the glass transition temperature toward the test temperatures in a manner which can account for the viscosity increases observed.

Problems in applying the Bagley and Rabinowitsch capillary corrections have been mentioned previously and will be only briefly reconsidered. For

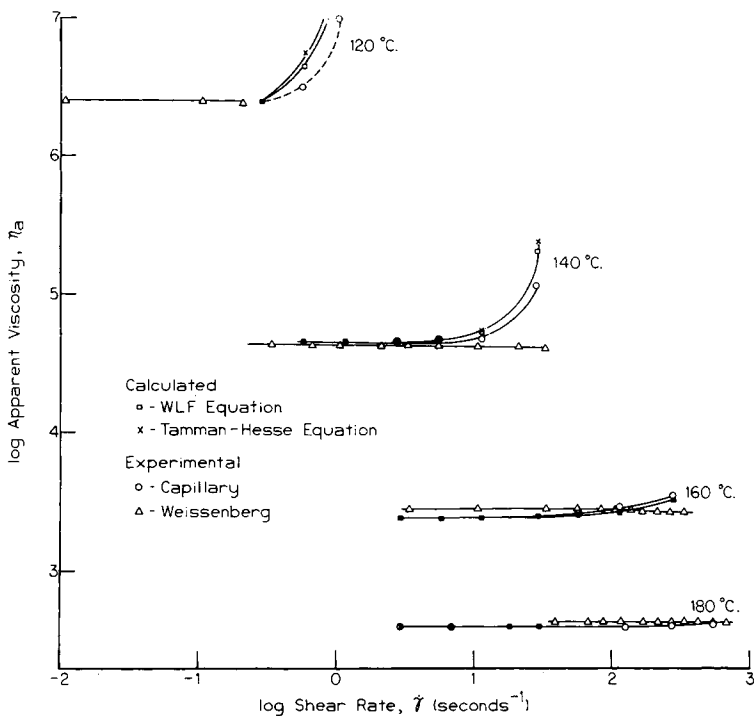


Fig. 4. Comparison of Weissenberg rheogoniometer and capillary flow data with calculated results for narrow-distribution low molecular weight polystyrene ($M_w = 20,400$; $M_w/M_n \leq 1.06$).

the high molecular weight polystyrene, both corrections are difficult to apply in the region where the viscosity increases with increasing shear rate. The Bagley plot is nonlinear which makes a linear extrapolation impossible. Also, it is not clear what deviations from parabolic flow may occur at high pressures, thus making a Rabinowitsch correction untenable. A possible solution to these difficulties might evolve from a consideration of Figure 5. In Figure 4 the experimental curve was duplicated semiquantitatively by calculating a viscosity increase and combining it with a suitable power law expression. An alternate approach would be to subtract the calculated

viscosity increase from the experimental curve giving the corrected curve in Figure 5. The resultant curve, which represents a pressure-corrected version of the experimental data, can be described by a power law expression over the entire range and the Rabinowitsch correction can nominally now be applied. This same pressure correction, applied to the low molecular weight polystyrenes, returns the experimental data to Newtonian behavior. Although this was not done, it seems reasonable to suggest that this same pressure correction, applied to a nonlinear Bagley plot, would result in linear curves. This would eliminate the difficulty imposed by a nonlinear plot and would make the correction possible for both the high and low molecular weight polystyrenes.

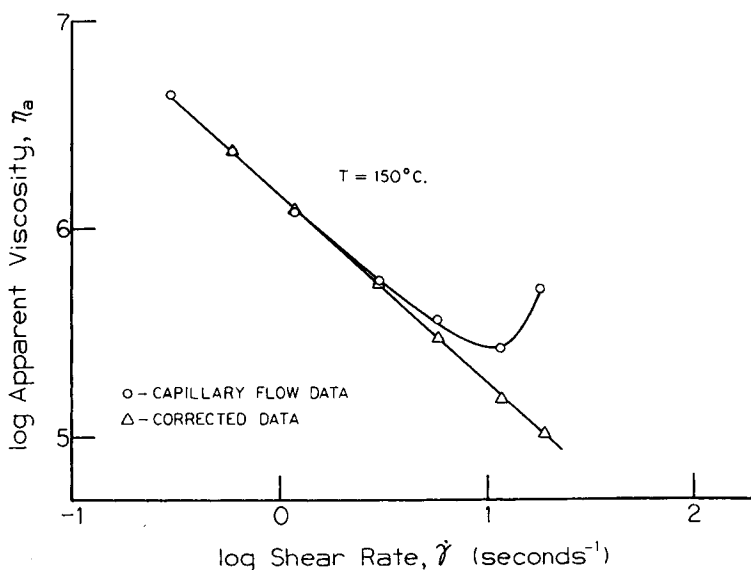


Fig. 5. Pressure correction of the apparent viscosity of the narrow-distribution high molecular weight polystyrene ($M_w = 670,000$; $M_w/M_n \leq 1.10$).

The study of variable capillary pressure has provided a quantitative explanation for the increase in apparent viscosity with shear rate from considerations of changes in free volume. Calculations, using independently the Tammann-Hesse and WLF equations coupled with Gee's pressure-versus- T_g relationship, agree well with experimental data on both high and low molecular weight polystyrenes. Comparisons with the Weissenberg data also support the idea that pressure reduces the free volume, which apparently shifts the glass transition 30° and more. This shift in T_g can account for the apparent viscosity increase with increasing shear rate. In the absence of pressure effects the low molecular weight polystyrene is Newtonian throughout the measurable shear rate range and the high molecular weight polystyrene obeys the power law at the higher rates of shear.

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