The Viscosity of Concentrated Polymer Solutions Containing Low Molecular Weight Solvents

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Synopsis

The zero shear rate viscosities of polystyrene/ethylbenzene solutions having polymer weight fractions ranging from 0.5 to 1.0 have been measured using a novel sealed rheometer cell over a temperature range of 50 to 200°C. The concentration and temperature dependence of the solution viscosity has been found to be well described by the relation $\eta_0 = K\,c^a\,M_w{}^{3.4}\zeta(c,T)$ where the monomeric friction coefficient ζ is determined by the free volume of the solution. Following the procedure of Berry, the free volume parameters, $\alpha_f(c)/\gamma$ and $T_\infty(c)$, and the fractional free volume, $f(c,T)/\gamma$, have been determined. After using these parameters to account for the concentration dependence of the friction coefficient, the concentration exponent a has been evaluated and found to be in reasonable agreement with the value of 3.4 obtained by Berry and Fox for other polymer/solvent systems. A comparison of the relative conributions made by the friction coefficient and the term $c^{3.4}$ to the overall concentration dependence of the viscosity of these highly concentrated solutions shows the friction coefficient to be the dominant factor.

INTRODUCTION

The rheological behavior of highly concentrated polymer solutions containing low molecular weight solvents is an important consideration in many polymer processing operations including bulk and solution polymerizations and polymer devolatilization processes. Considerable attention has been given to the determination of the temperature and molecular weight dependence of the zero shear rate viscosity of polymer solutions and melts. Relatively little effort, on the other hand, has been devoted to evaluating the concentration dependence of the viscosity of highly concentrated polymer solutions. Both experimental and theoretical studies suggest that the zero shear rate viscosity η_0 for concentrated solutions of linear, flexible polymers can be expressed in the following manner[1-4]:

$$\eta_0 = K\,c^{\bar{a}}\overline{M_w}^{\,\bar{b}}\zeta \tag{1}$$

where

$$\bar{b} = 1.0 \text{ for } \phi_2\overline{M_w} < M_c \tag{2}$$

$$\bar{b} = 3.4 \text{ for } \phi_2\overline{M_w} > M_c \tag{3}$$

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where K is a constant for a given polymer, c is the polymer concentration, $\overline{M}_w$ is the weight average molecular weight of the polymer, ζ is the segmental friction coefficient, M_c is the critical molecular weight for entanglement, and ϕ_2 is the polymer volume fraction.

The friction factor ζ is a measure of the resistance encountered by the polymer molecule as it undergoes translational motion through the surrounding medium. It is dependent on both temperature and concentration, but it is essentially independent of the polymer molecular weight provided the molecular weight of the polymer is large. Graessley[3] suggests that ζ is independent of molecular weight if the number average molecular weight is greater than 10,000.

The concentration exponent $\overline{a}$ can only be determined after one has accounted for the concentration dependence of ζ. In the few studies in which this concentration dependence has been estimated, values of $\overline{a}$ ranging from 3.4 to 6.3 have been reported in the region above the critical molecular weight.[1,5-10] The variability in the values obtained for $\overline{a}$ can be at least partially attributed to differences in the methods used to estimate the concentration dependence of the friction coefficient, they differ in the procedure used to evaluate the concentration dependence of the free volume.

An expression for the friction coefficient based on free volume concepts can be derived from the empirical Doolittle equation[11]:

$$\zeta = \zeta_0 \exp(\gamma/f) \tag{4}$$

where ζ_0 and γ are assumed to be constants. The fractional free volume f is defined as the ratio of the free volume to the occupied volume. A theoretical basis for the use of eq. (4) has been provided by Cohen and Turnbull.[12] The temperature dependence of f can be described in terms of the Vogel temperature T_∞[13]

$$f(T) = \alpha_f(T - T_\infty) \tag{5}$$

The Vogel temperature refers to the point at which f would go to zero in the absence of the glass transition. Equation (4), with f defined by eq. (5), provides a satisfactory description of the temperature dependence of ζ for polymer melts and solutions as well as low molecular weight liquids for a limited region above T_g. At temperatures far above T_g, ζ has been found to be better described by an Arrhenius temperature dependence.

The concentration dependence of the friction coefficient has not been as clearly established as its temperature dependence. In general, the concentration dependence of f depends on the properties of the pure components and specific interactions which occur between the components. Kelley and Bueche,[9] in a study of the viscosity of concentrated polystyrene/diethylbenzene and poly(methyl methacrylate)/diethyl phthalate solutions, assumed the fractional free volumes of the polymer and solvent to be additive, i. e.,

$$f(\phi,T) = \phi_1\alpha_{1f}(T - T_{1\infty}) + \phi_2\alpha_{2f}(T - T_{2\infty}) \tag{6}$$

where the subscripts 1 and 2 refer to the solvent and polymer, respectively.

They found that the concentration dependence of η_0 for these solutions could be satisfactorily correlated by using the above expression for $f(\phi,T)$ along with a value of 4.0 for the concentration exponent $\bar{a}$ in eq. (1). The same approach was used by Pezzin[10] to account for the concentration dependence of the viscosity of several polymer/solvent systems including solutions of polyisobutylene in isooctane and poly(ethyl methacrylate) in diethyl phthalate. Mendelson[6] evaluated the exponent $\bar{a}$ in eq. (1) explicitly for polystyrene/ethylbenzene solutions after using eq. (6) to estimate $f(c,T)$ and obtained a value of 6.3.

An expression for $f(\phi,T)$ which includes an interaction term to account for the free volume change of mixing has been proposed by Braun and Kovacs[14]:

$$f(\phi,T) = \phi_1\alpha_{1f}(T-T_{1\infty}) + \phi_2\alpha_{2f}(T-T_{2\infty}) - C\phi_1\phi_2 \qquad (7)$$

where C is constant. Equation (7) was used by Braun and Kovacs in deriving a free volume relation for the concentration dependence of the glass transition temperature of polymer solutions. Marin et al.,[7] in a study of the rheological properties of narrow molecular distribution polybutadienes in an aromatic oil, used eq. (7) to estimate $f(\phi,T)$ with the constant C determined from T_g measurements. After accounting for the concentration dependence of f in this manner, the exponent $\bar{a}$ in eq. (1) was determined to be 4.0.

Berry[5] determined the concentration dependence of the free volume parameters, α_f and T_∞, for solutions of polystyrene in dibenzyl ether directly from the experimentally determined temperature dependence of the solution viscosities, thus avoiding the necessity to assume a form for $f(c)$. After using the free volume parameters to evaluate the conceration dependence of the friction coefficient, Berry obtained a value of 3.4 for the concentration exponent $\bar{a}$ in eq. (1). In subsequent studies by Berry and co-workers using the same reduction procedure for other polymer/solvent systems, the value of $\bar{a}$ was also determined to be 3.4.[1,8]

With the exception of Berry's work, the investigations cited above all assumed a form for the concentration dependence of the fractional free volume. In some cases an assumed value of the exponent $\bar{a}$ was also used.[9,10] Recent theoretical and experimental studies dealing with diffusion in concentrated polymer solutions[15,16] suggest that the solvent size has a significant effect on the concentration dependence of the friction coefficient. Thus, polymer solutions containing low molecular weight solvents of industrial importance may exhibit rheological behavior which is quite different from polymer solutions containing the high molecular weight solvents used in many previous studies. The results of Mendelson[6] suggest that significant differences do exist between the concentration dependence of the viscosity of solutions containing high and low molecular weight solvents. It is not clear, however, whether these differences are attributable to differences in the concentration dependence of ζ, the value of the concentration exponent, $\bar{a}$, or both of these factors since the concentration dependence of ζ was not evaluated explicitly.

In this study, the concentration dependence of the fractional free volume, and thus ζ, for concentrated polystyrene/ethylbenzene solutions is deter-

mined using the procedure described by Berry.[5] By evaluating $f(c)$ in this manner, the validity of the additivity assumption for these solutions can be examined and an unambiguous determination of the value of $\bar{\alpha}$ in eq. (1) can be made. The results obtained here for ethylbenzene will be compared to those obtained by Berry for solutions with higher molecular weight solvents.

EXPERIMENTAL

In the current study two polystyrene samples were used: one a broad molecular weight distribution polymer having an $\bar{M}_w = 271{,}000$, and the other a narrow molecular weight distribution sample having an $\bar{M}_w = 690{,}000$. These polymers will be subsequently referred to as PS271 and PS690, respectively. The ethylbenzene used was a Fischer Certified Grade obtained from the Fisher Scientific Co. (Chemical Manufacturing Division, Fairlawn, NJ). Viscosity measurements were made on polystyrene/ethylbenzene solutions having polymer weight fractions ranging from 0.5 to 1.0. Thus, the concentrations and molecular weights used were sufficiently high to ensure that the values of $\phi_2 \bar{M}_w$ were well above the critical molecular weight for entanglement in all cases. For polystyrene M_c is approximately 35,000.[2]

Viscosity measurements on the polystyrene/ethylbenzene solutions were made at temperatures ranging from 50 to 200°C. Because ethylbenzene is normally highly volatile in this temperature range, these measurements were performed in a specially designed sealed parallel plate rheometer cell. This rheometer cell is able to perform both steady state and dynamic rheological measurements in a controlled environment and at elevated temperatures and pressures. It is designed to mount onto either a Rheometrics Mechanical Spectrometer or a Rheometrics System Four rheometer (Rheometrics, Inc., Piscataway, NJ). The rheometer cell utilizes the drives, control systems, and data acquisition facilities of these instruments, and is therefore able to operate over a wide range of shear rates and frequencies. The details of the design and operating characteristics of the rheometer cell have been described elsewhere.[17,18] The lower plate of the rheometer is actually a shallow cup which can be detached from the transducer. Several of these cups were produced for the rheometer cell and used during the preparation of the samples as described below.

For the viscosity measurments on the polystyrene melts, disks of the samples were prepared in a vacuum mold. The highly concentrated polystyrene/ethylbenzene solutions used in this study were obtained by evaporating solvent from solutions of lower concentration. The low concentration solutions were prepared by adding prescribed quantities of the polystyrene and ethylbenzene into a preweighed beaker. The solutions were mixed for several hours on a hotplate set at approximately 50°C. Additional ethylbenzene was added periodically to make up for solvent losses due to evaporation. Once the dissolution of the polystyrene was complete, the mixture was weighed directly into the shallow cups which serve as the lower plates of the rheometer cell. Small quantities of the initial solutions were also weighed into aluminum dishes and dried in a vacuum oven in order to accurately determine the initial polymer concentrations.

The shallow cups containing the initial solution were placed in a vacuum oven, and the weight loss of ethylbenzene from each cup was monitored. When the desired final concentration was approached, the cup was sealed using a specially designed lid. The solution was then allowed to equilibrate for 1–3 days, depending on the sample concentration, in order to eliminate concentration gradients developed during the evaporation process. Just prior to inserting the sample cups into the rheometer cell, they were weighed to obtain a final value for the polystyrene concentration.

For the measurements reported here, the rheometer cell was mounted onto a Rheometrics System Four rheometer. All measurements were made in the steady state mode in this study because the wide range of shear rates available permitted the determination of the zero shear rate viscosity over a much broader temperature range than could be obtained from dynamic measurements. After the shallow cup containing the sample was mounted in the rheometer cell, the cell was sealed and filled with glycerin. The glycerin, a nonsolvent for the ethylbenzene, provided the controlled environment necessary to maintain a constant sample concentration. The rheometer cell was hydraulically pressurized as necessary to prevent the ethylbenzene from vaporizing. The maximum pressure used during the tests was 6 atm, which is not large enough to significantly affect the viscosity. The viscosity measurements were made over approximately a decade of shear rate to ensure that the low shear rate limiting value of the viscosity had indeed been obtained. Further details of the experimental procedures are available elsewhere.[18]

RESULTS AND DISCUSSION

The temperature dependence of the zero shear rate viscosity for polystyrene/ethylbenzene solutions at several concentrations is shown in Figure 1 for PS271 and in Figure 2 for PS690. With the possible exception of the lowest concentration PS690 solution, the temperature depnedence of η_0 for all the solutions show a marked deviation from an Arrhenius type behavior.

The concentration dependence of the viscosity for the PS271 solutions is shown more explicitly in Figure 3, where logarithmic plots of η_0 vs. c at several temperatures have been constructed from the data in Figure 1. The plots include solution concentrations ranging from approximately 50% polymer to the melt. It is apparent form these plots that the zero shear rate viscosity of these highly concentrated solutions is a very strong function of the concentration. At the highest concentrations, for example, the slopes of the curves, $d \log \eta_0 / d \log c$, approach values greater than 30. In this region the concentration dependence of η_0 is clearly dominated by the concentration dependence of ζ rather than the concentration term shown explicitly in eq. (1). It is quite reasonable to expect, therefore, that the technique used to evaluate $\zeta(c)$ will have a strong influence on the value obtained for the concentration exponent $\bar{a}$ in eq. (1). It should also be apparent that for these highly concentrated systems errors introduced in the prediction of η_0 due to small differences in the exponent $\bar{a}$ will be relatively minor in comparison to the errors that may be introduced by inaccurate estimates of $\zeta(c)$. By using the technique suggested by Berry[5] to determine the concentration dependence of the free volume parameters, and thus the
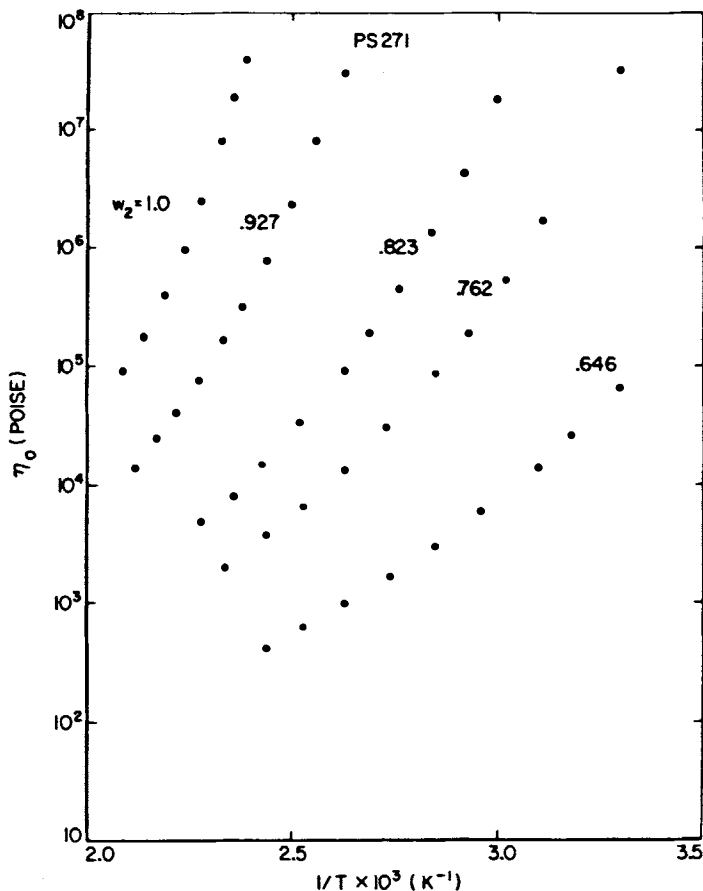
Fig. 1. Temperature dependence of the zero shear rate viscosity for PS271/ethylbenzene solutions at several polymer weight fractions. The viscosities were determined from steady state measurements in the sealed rheometer cell.

friction coefficient, directly from the viscosity data, the need to assume a form for $\zeta(c)$ is eliminated. Once the concentration dependence of the friction coefficient is known, an evaluation of the exponent $\bar{a}$ can be easily made. This approach has been used to analyse the viscosity data presented here.

From eqs. (1), (4), and (5), it can be seen that the ratio of the viscosity at a temperature T to the viscosity at a reference temperature T_s is

$$\ln \frac{\eta_0(T)}{\eta_0(T_s)} = \frac{\gamma}{\alpha_f} \left[\frac{1}{(T-T_\infty)} - \frac{1}{(T_s-T_\infty)} \right] \qquad (8)$$

By rearranging the above equation one obtains

$$\frac{-(T-T_s)}{\ln[\eta_0(T)/\eta_0(T_s)]} = \frac{\alpha_f}{\gamma} (T_s-T_\infty)[(T-T_s) + (T_s-T_\infty)] \qquad (9)$$

The free volume parameters, α_f/γ and T_∞, can therefore be determined
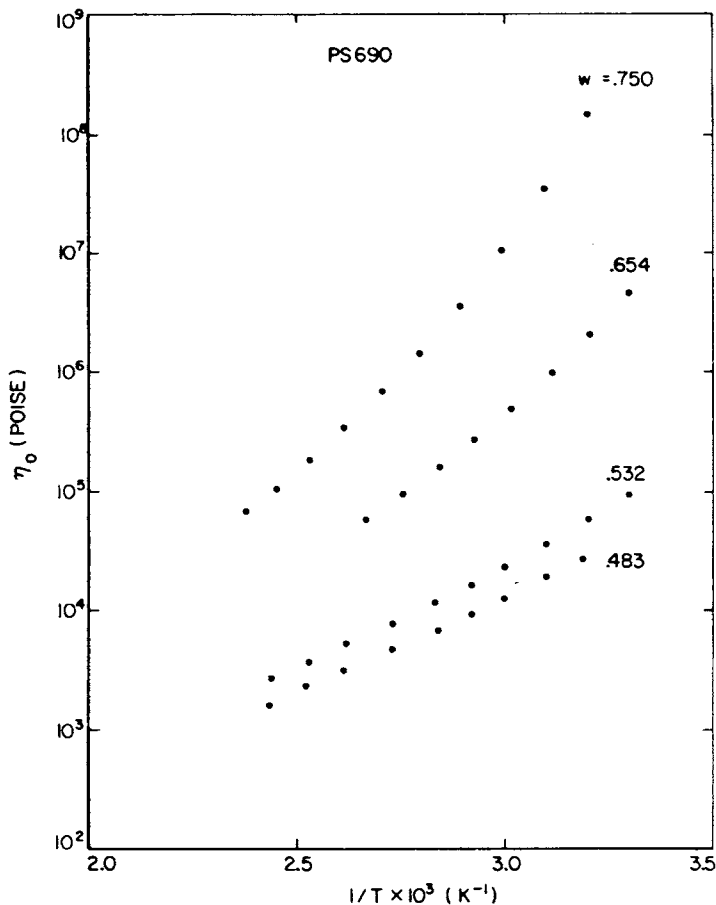
Fig. 2. Temperature dependence of the zero shear rate viscosity for PS690/ethylbenzene solutions at several polymer weight fractions. The viscosities were determined from steady state measurements in the sealed rheometer cell.

from the slope m and intercept i of a plot of $\{-(T-T_s)/\ln[\eta_0(T)/\eta_0(T_s)]\}$ vs. $(T-T_s)$ as follows:

$$\alpha_f/\gamma = m^2/i \tag{10}$$

$$T_\infty = T_s - i/m \tag{11}$$

The data for the PS271 solutions are plotted in the above manner in Figures 4 and 5. In Figure 4 the data reduction procedure has been performed using the lowest temperature at which measruements were made for each polymer solution as the reference temperatrue. In Figure 5 the procedure has been repeated using the highest temperature of measurement for T_s. Agreement between the values of the free volume parameters calculated using the two extreme reference temperatures is required in order to ensure that the free volume description of $\zeta(T)$ is valid over the entirè temperature range. It is evident that for each set of data shown in these figures the plots are linear and the amount of scatter is slight. Similar results were obtained for the
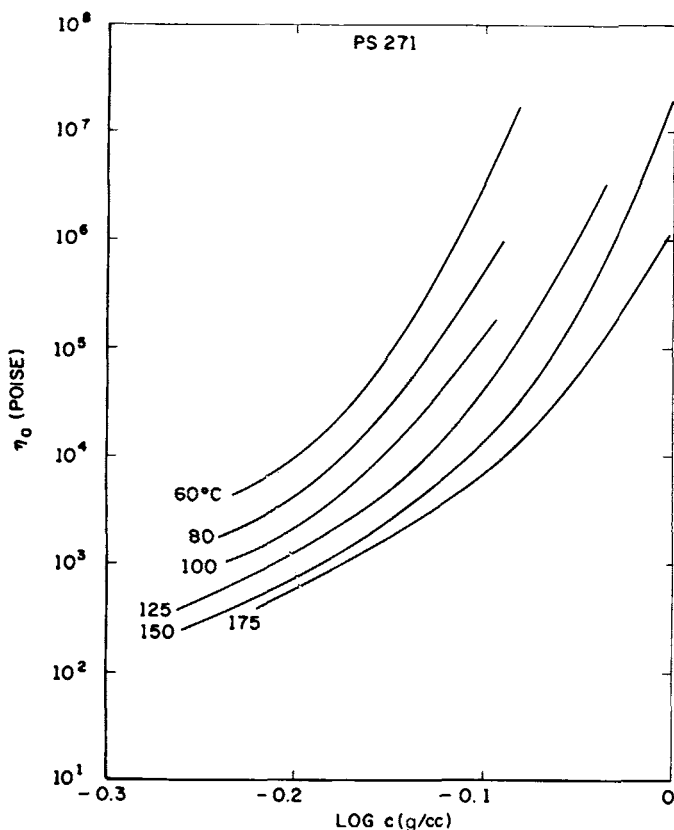
Fig. 3. Concentration dependence of the zero shear rate viscosity for PS271/ethylbenzene solutions.

three highest concentration PS690 solutions. The procedure was not able to be successfully applied to the lowest concentration PS690 solution. Apparently, in the temperature range where the viscosity measurements were made, this solution was too far above its glass transition temperature for free volume effects to be the controlling factor. With the exception of the lowest concentration PS690 solution, correlation coefficients of 0.9995 or better were obtained in all cases. In addition, for each solution the agreement between the values of the parameters α_f/γ and T_∞ calculated using the two extreme reference temperatures was found to be within 3%. These results indicate that for these solutions the temperature dependence of the friction coefficient is well described by eq. (4) over the entire temperature and concentration range considered.

The values of the free volume parameters obtained from the reduction procedure are given in Table I and are plotted as a function of the polymer weight fraction w_2 in Figures 6 and 7. The free volume parameters for pure ethylbenzene are also given. These values were calculated by Duda et al.[16] from the viscosity data of Barlow et al.[19] No distinction has been made between the free volume parameters obtained from the PS271 solutions
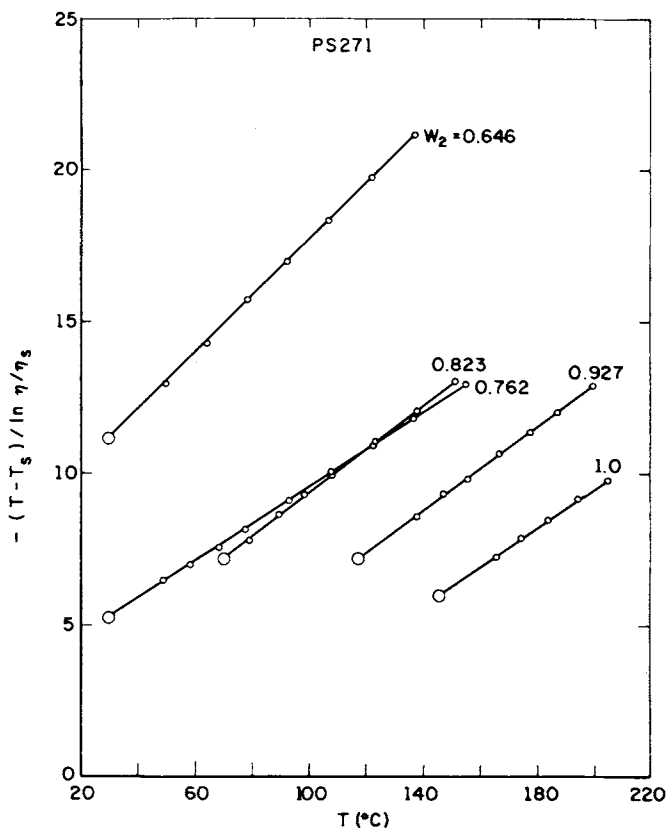
Fig. 4. The temperature dependence of the viscosity of PS271 solutions is used to determine the free volume parameters. The parameters are calculated for each concentration from the slope of the line and the line's intersection with the reference temperature T_s. The value of T_s used at each concentration is indicated by the large circles. In this plot the lowest temperatures have been used for T_s.

and those obtained from the PS690 solutions since they should be independent of molecular weight and molecular weight distribution for the high molecular weights and concentrations used in this study. The values of the free volume parameters obtained for pure polystyrene are in good agreement with the values of 6.9×10^{-4} K^{-1} and 325 K suggested by Ferry for α_f/γ and T_∞, respectively.[2]

It can be seen from Figure 6 that α_f/γ increases slightly with decreasing polymer concentration. However, at 50 wt % polymer the value of α_f/γ is still far removed from the value determined for pure ethylbenzene. In contrast, T_∞ initially decreases very rapidly with decreasing polymer concentration and eventually approaches the value of T_∞ for pure ethylbenzene. These results indicate that the large decrease in viscosity obtained when small quantities of a low molecular weight solvent are added to the polymer melt can be primarily attributed to a reduction in T_∞.

The concentration dependence of the fractional free volume at any temperature can be calculated using eq. (5) along with the values of the free
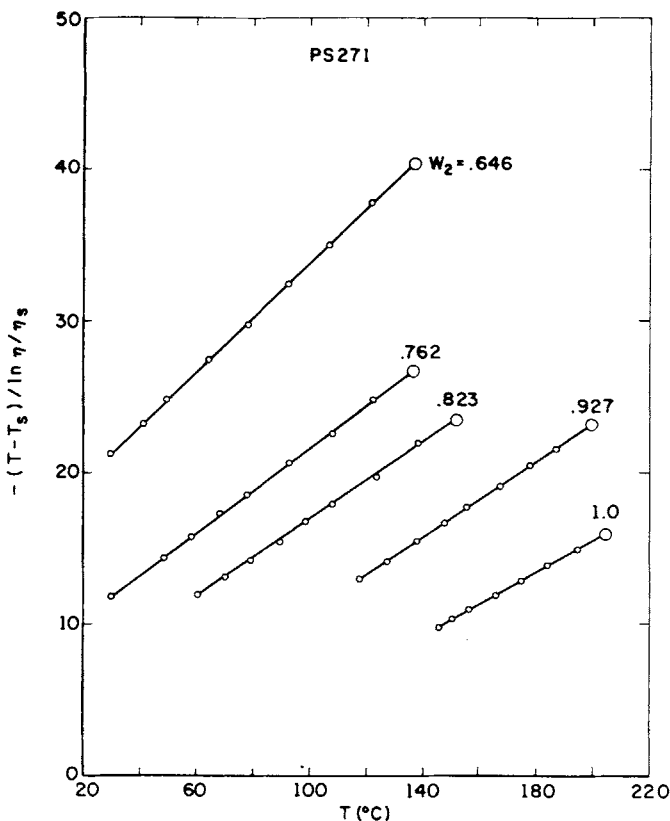
Fig. 5. The reduction scheme is shown for PS271 solutions with the highest temperatures used for T_s.

volume parameters in Table I. In Figure 8, f/γ is shown as a function of polymer weight fraction at temperatures of 50, 100, and 150°C. At all three temperatures f/γ increases approximately linearly with decreasing w_2. However, extrapolation of these lines to the point where $w_2 = 0$ gives values for f/γ which are significantly less those obtained for pure ethylbenzene, indicating that for this polymer/solvent system the fractional free

TABLE I
Free Volume Parameters For Polystyrene/Ethylbenzene Solutions

w_2	α_f/γ (K^{-1})	T_∞ (K)
1.0	6.86×10^{-4}	325
0.927	6.80×10^{-4}	288
0.823	7.01×10^{-4}	241.5
0.762	7.28×10^{-4}	218.5
0.750	7.20×10^{-4}	216.5
0.654	7.40×10^{-4}	185.5
0.646	7.92×10^{-4}	185
0.532	7.92×10^{-4}	152.5
0[a]	21.7×10^{-4}	95

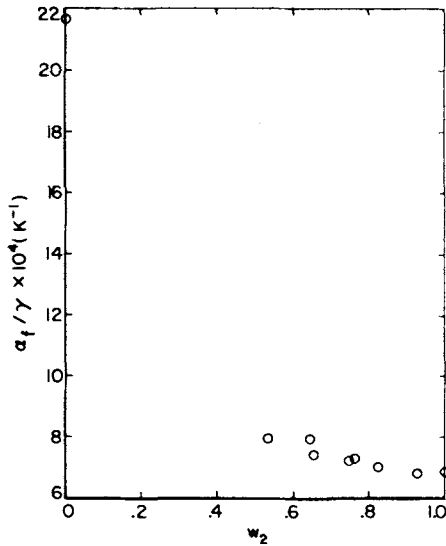[a] Values for pure ethylbenzene are those obtained by Duda et al.[16] from data of Barlow et al.[19]

Fig. 6.   Concentration dependence of the fractional free volume thermal expansion coefficient for polystyrene/ethylbenzene solutions.

volume is not additive. A more detailed evaluation of the concentration dependence of the free volume will be the subject of a future paper.

The small values of f/γ which are found in the temperature and concentration range employed in this study account for the strong dependence of the viscosity on changes in the temperature and concentration. Since the viscosity is proportional to the exponential of the inverse of f/γ, any changes in f/γ at these small values will have a significant effect on η_0.

With the concentration dependence of f/γ, and therefore ζ, known, the concentration exponent $\bar{a}$ in eq. (1) can be determined from a logarithmic
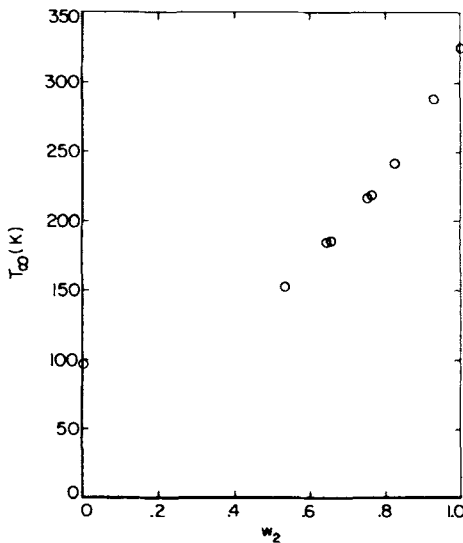

Fig. 7.   Concentration dependence of the Vogel temperature for polystyrene/ethylbenzene solutions.
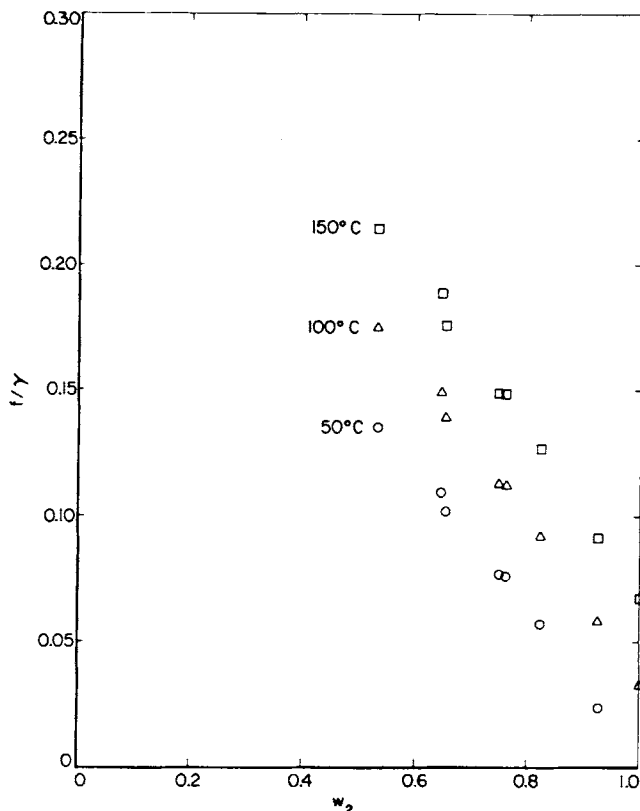
Fig. 8. Concentration dependence of the fractional free volume for polysytrene/ethylben-zene solutions.

plot of the reduced viscosity η_{red} vs. concentration, where the reduced viscosity is defined as

$$\eta_{red} = \eta_0/\exp(\gamma/f) \tag{12}$$

For each molecular weight the plot should be linear with a slope equal to $\bar{a}$. In Figure 9 the viscosity data for the PS271 and PS690 solutions are plotted in this manner. The points on the plot represent the average of the reduced viscosities obtained at al the temperaures at which measurements were made for each solution, i. e., each point represents several experimental measurements. The deviation from the average value was less than 4% in all cases. The viscosity measurements for each solution were made at a constant polymer weight fraction rather than constant concentration. Because the thermal expansion coefficients of polystyrene and ethylbenzene are not equal, the concentration of the solutions did vary to some extent with temperature. The concentrations used in Figure 9 are values calculated at the midpoint of the temperature range used for each solution.

Linear regression analyses of the two sets of data in Figure 9 yield a slope of 3.0 for the PS271 solutions and 3.3 for the PS690 solutions. It can be
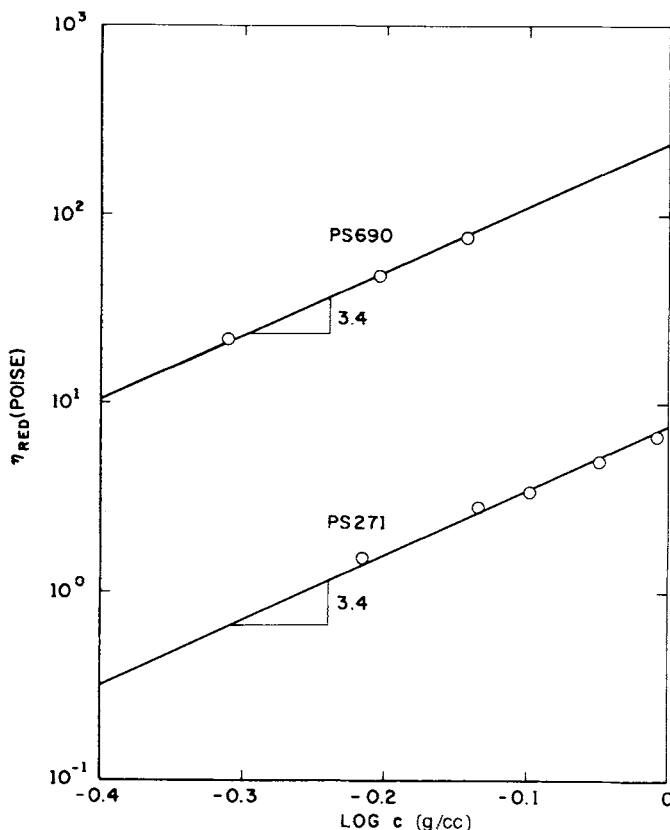
Fig. 9. Concentration dependence of the reduced zero shear rate viscosity for polystyrene/ethylbenzene solutions. A slope of 3.4 provides a satisfactory correlation of the data.

seen from Figure 9, however, that lines of slope 3.4 correlate both sets of data quite well. The value of 3. 4 has been reported by Berry and Fox for several polymer/solvent systems.[1] The reduction procedure used here to evaluate the friction factor, and subsequently the concentration exponent $\bar{a}$, is very sensitive to experimental errors. Accurate data over a wide range of temperature and concentration are required in order to obtain a reliable value for the exponent $\bar{a}$. This requirement is particularly important for polymer solutions containing low molecular weight solvents because the concentration dependence of the viscosity is dominated by the concentration dependence of the friction coefficient. In this study, data were taken over a large portion of the concentration and temperature region in which free volume effects are controlling. The viscosities vary by more than 5 orders of magnitude in the concentration range studied. However, after correcting the data to account for the strong concentration dependence of the friction factor, the reduced viscosities vary by less than 1 order of magnitude. Therefore, even small experimental errors or errors introduced during data analysis may be of sufficient magnitude to account for the differences in the concentration exponent obtained here and the value of 3.4 reported by Berry and Fox.

CONCLUSIONS

The zero shear rate viscosity of highly concentrated polystyrene/ethylbenzene solutions has been found to be very sensitive to changes in concentration. This sensitivity is largely a result of variations in the fractional free volume with concentration. Direct measurement of the concentration dependence of the fractional free volume shows that the assumption of additivity considerably overestimates the fractional free volume of these solutions. This result is in qualitative agreement with the results obtained by Duda et al.[16] in studies of diffusion in molecular weight solvents. After properly accounting for the concentration dependence of the friction coefficient, the value obtained for the concentration exponent in eq. (1) is in agreement with the value of 3.4 reported by Berry for other polymer solutions containing higher molecular solvents. It appears, therefore, that the exponent $\bar{a}$ is not dependent on the type of solvent and that variations in the concentration dependence of the zero shear rate viscosity of a polymer with different solvents is due solely to differences in the concentration dependence of the fractional free volumes of these solutions.

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