A Unifying Approach for Melt Rheology of Linear Polystyrene

Sung Hun Kim,[1] Fouad Teymour,[1] Jon A. Debling[2]

[1]Department of Chemical Engineering, Illinois Institute of Technology, Chicago, Illinois 60616
[2]Johnson Polymer, 8310 16th Street, PO Box 902, Sturtevant, Wisconsin 53177

ABSTRACT: Several studies of melt rheological properties of polystyrene have been conducted over the past 50 years. Several approaches, including empirical models, have been developed to understand the behavior of materials using simple equations. The existing melt rheology models are best suited for high-molecular-weight polymers whose T_g does not vary. In this work, a semiempirical viscosity equation has been derived, including the effect of T_g dependence on molecular weight, to describe the melt rheology of low-molecular-weight polymers. The equation is derived based on a combination of well-known concepts, such as the effects of free volume and molecular dynamics on polymer rheology. This provides a better understanding of the rheological behavior in the low-molecular-weight regime with respect to temperature and molecular weight. Because of the industrial trend towards lower molecular weight materials for applications such as high solids coatings, this unifying approach, based on the free volume theory with a simple expression, is of extreme practical significance. This equation can predict the zero shear viscosity behavior for different molecular weights, including low-molecular-weight regions, and temperatures. Viscosity calculations using the empirical equation agree with published experimental data. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2597–2607, 2007

Key words: polystyrene; melt; viscosity; rheology; oligomers

INTRODUCTION

The viscosity behavior of linear polymers has been studied extensively. Several empirical and semiempirical models and approaches have been suggested.[1] The effects of molecular weight (MW) and temperature on rheological behavior have been the main focus of most studies. The theory is well developed for the MW dependence of melt viscosity in isothermal measurements for high-MW polymers, while major deviations have been observed for low-MW polymers.[2–9] Increased industrial attention to low-molecular-weight resins, for applications such as high solids coatings, pigment dispersants, printing inks, etc., is starting to gradually shift the attention of researchers to the behavior of low-MW polymers.[10,11]

For polymers with sufficiently high MW, a logarithmic plot of the melt viscosity versus molecular weight universally exhibits a slope of 1.0 up to a certain critical MW, M_c, then a slope of ~ 3.4 above M_c. In contrast, for low-molecular-weight polymers, isothermal measurements below M_c reflect a curvature that only approaches unity as M_c is approached.[2,3] This behavior is a result of the dependence of the glass transition temperature (T_g; or more fundamentally "fractional free volume") on MW, an effect that

is magnified at low MW because of the increased sensitivity of T_g to MW for these materials. Thus, not only the MW dependence, but also the free volume contribution, should be clarified to develop the complete picture of the melt viscosity behavior over wide ranges of MW and temperature.

Fortunately, different theories have already been developed and applied to describe the effect of various separate characteristics on the polymer physical properties.[2,12–15] In this article, an attempt is made to develop a unified approach, based on the free volume theory, which is significantly correlated with the T_g and viscosity behaviors, to predict zero shear melt viscosity over wide ranges of MW and temperature.

One major contribution of MW dependence to the observed deviations for low-MW polymers is related to T_g. The glass transition temperature, $T_g(M)$, is a strong function of M, molecular weight, especially when $M < M_c$, since the "excess free volume" of the chain ends plays a major role at very low MWs.[16] As a result, for low-MW polymers, the viscosity has to be compared at the "normalized" temperature $(T - T_g)$ and not just the same T. This normalization ensures a comparison at "isofree volume" conditions and allows the decoupling of free volume effects from MW effects.

Another contribution of the dependence to MW in a unifying approach can be illustrated by two expressions: (i) the Rouse model and (ii) the Reptation model.[3,17] The viscoelastic properties of low-MW polymers and the transition to the entangled re-

Correspondence to: F. Teymour (teymour@iit.edu).

gime have been investigated using these different models. The crossover region between the unentangled and entangled regimes is located at the critical molecular weight, M_c.[3,17]

In general, because of significant free volume change in the low-MW region, isofree volume conditions should be ensured. As mentioned previously, for isothermal measurement in the low-MW region, the slope of melt viscosity versus MW is not constant. To explain that qualitatively and quantitatively, free volume theory can be utilized to determine a simple semiempirical equation that adequately describes the viscosity behavior of polymers. In this sense, Colby et al.[2] have already suggested that the viscosity of polymer liquids can be represented as the product of a structural factor, F, and a friction coefficient, ζ, as in

$$\eta_o = F(M)\zeta(f(T)) \tag{1}$$

The structural factor for linear polymers depends on chain length (or MW) but is insensitive to temperature.[2,18–20] The friction coefficient, on the other hand, reflects the local dynamics and governs the temperature dependence of viscosity.[2,18–21] The friction coefficient can be related to the concentration of chain ends (or fractional free volume), which follows the T_g behavior, the effect of which diminishes with increasing MW. As a result, the temperature dependence of viscosity is only correlated to the temperature dependence of fractional free volume which can be described using WLF (Williams-Landel-Ferry) type approach in details.

In what follows, we review the previously developed background theories, then demonstrate how these can be integrated to yield a unified approach capable of describing viscosity behavior over the wide MW and temperature ranges.

Theoretical development

Free volume theory and glass transition

Many of the properties of liquids reflect the presence of a substantial proportion of free volume, which may be present as holes on the order of molecular dimensions or smaller voids associated with packing irregularities.[22] This free volume is distributed at random within the amorphous phase and there is a contribution to the entropy from this randomness,[23–31] which is not present in the entropy of a crystalline phase. The appearance of holes lowers the density of the amorphous polymer by about 10% as compared to the crystalline state of the same material.[26,27] The free volume associated with chain ends is generally greater than that associated with the chain backbone because of imperfect packing at the chain ends. Thus the dependence of T_g on MW diminishes at high molecular

weight, as the concentration of chain ends becomes negligible. On the other hand, free volume increases with temperature as a result of thermal expansion. This can be expressed by the empirical correlation[22,32,33]

$$f = f_g + \alpha_f(T - T_g) \tag{2}$$

which relates the fractional free volume (f) to temperature, where f_g is the fractional free volume at T_g, and α_f the expansion coefficient of the polymer. Additionally, at any particular temperature, the dependence of free volume on chain end concentration, which for linear polymers is strictly proportional to MW, can be expressed according to the following empirical correlation[22,32–36]:

$$f_M = f_\infty + \frac{2K}{M_n} \tag{3}$$

where f_M and f_∞ are the fractional free volumes for a molecular weight, M, and infinitely large molecular weight, respectively, K is constant, and M_n is the number–average molecular weight (M_n). The dependence of f_M and f_∞ on temperature, according to eq. (2), are expressed as

$$f_M = f_g + \alpha_f(T - T_{gM}) \tag{4}$$

$$f_\infty = f_g + \alpha_f(T - T_{g\infty}) \tag{5}$$

Inserting these expressions into eq. (3) and rearranging yields an expression correlating T_g to MW.

$$T_{gM} = T_{g\infty} - \frac{2K}{\alpha_f}\frac{1}{M_n} \tag{6}$$

This equation has been shown to work well for narrow linear polymers.[22,32,33] In eq. (6), T_{gM} and $T_{g\infty}$ are the glass transition temperatures at a MW, M, and for "infinite" molecular weight. As shown here as well as previously, free volume, and consequently T_g, are strongly dependent on the M_n.

Viscosity and free volume

The relationship between viscosity and free volume is generally expressed by the Doolittle equation and the WLF equation. The Doolittle equation is given by

$$\ln \eta = A + \frac{b}{f} \tag{7}$$

where A and b are assumed constants. The WLF (Williams-Landel-Ferry) equation is an analytical relationship between polymer melt viscosity and free volume,[37] derived from the Doolittle equation.[38–41]

$$\ln\left(\frac{\eta}{\eta_g}\right) = -\frac{(b/f_g)(T - T_g)}{f_g/\alpha_f + (T - T_g)} \tag{8}$$

Where b = constant, η = viscosity, η_g = viscosity at T_g, α_f = thermal expansion coefficient, and f_g = the fractional free volume at T_g, the parameters of eq. (8), as used by WLF,[37] are based on experimental observations found in the literature. They assigned a value of unity for the parameter "b", consistent with the viscosity data of Doolittle, and a universal value for f_g. This finding is significant in that it implies that the value of the free volume at T_g of any polymer is 2.5%. It must be emphasized that the validity of the WLF equation is reported to be in the range T_g to $T_g + 100$ (°C).[22,32,33,37]

Despite their success in describing the viscosity behavior of various polymeric materials, the Doolittle and the WLF equations have some limitations. It should be noted that these approaches have been examined only with assumptions of no MW dependence (in the Doolittle equation) and a constant value of viscosity at T_g (in the WLF equation). Since the Doolittle equation is empirical and mainly developed for small chain and simple liquids, it does not include the MW dependence effect. It was rather developed to reflect only the temperature effect on viscosity. This results in a considerable limitation for general application to polymeric materials. The second limitation is the necessity to know the viscosity at T_g in the WLF equation before it can be applied. The WLF equation can be utilized to calculate the viscosity at different temperatures, if the viscosity at T_g, which depends on MW, is evaluated correctly. The dependence of the viscosity at T_g is explored later in this article. First, we should also note that a generalized expression for free volume dependence on both MW and temperature can be obtained by combining eqs. (3) and (5). The resulting equation, eq. (9), is essential to the development of the unified approach described in this article, as shown later.

$$f(M_n, T) = f_g + \alpha_f(T - T_{g\infty}) + \frac{2K}{M_n} \tag{9}$$

Thus, the WLF equation can be modified to include the MW dependence given by eq. (9). Combining the Doolittle equation with the free volume expression in eq. (9) leads to the modified WLF equation given by

$$\ln\left(\frac{\eta}{\eta_g}\right) = -\frac{\left(\frac{b}{f_g}\right)(T - T_{g\infty}) + \left(\frac{b}{f_g}\right)\left(\frac{2K}{\alpha_f M_n}\right)}{\frac{f_g}{\alpha_f} + (T - T_{g\infty}) + \frac{2K}{\alpha_f M_n}} \tag{10}$$

This equation is essentially the same as the original WLF equation with the exception that it incorporates the effect of MW on free volume and consequently T_g. In general, this modified equation is only impor-

tant for polymers of low to intermediate MWs. This is a direct result of the T_g behavior versus MW, as it reaches a plateau value of $T_{g\infty}$ at sufficiently large MW, when chain end effects cease to be significant. One should note that, when eq. (10) is considered in the limit of "infinite" MW, it reduces to the original WLF equation in a manner consistent with these arguments.

Development of a unified equation for melt viscosity

As stated earlier, the objective of this article is to develop an approach that can reconcile a number of literature observations[3–9] that have been previously classified as deviations from the traditional theory. The MW contribution to free volume is correlated to M_n, while the MW effect on viscosity is usually represented by the weight–average molecular weight (M_w). It is generally observed by theories that the dependence of viscosity on the M_w follows a power law representation as given by

$$\eta = K'M_w^a \tag{11}$$

which can also be represented in logarithmic form as

$$\ln \eta = \ln K' + a \ln M_w \tag{12}$$

It is further observed that melt viscosity data, when plotted according to eq. (12), exhibit two distinct regions in which the values of the slope "a" are vastly different and distinct. According to the theories, at MWs below the critical molecular weight, M_c, where polymer chains are unentangled, this slope is equal to 1.0; while, above M_c, where entanglements dominate, the slope changes to 3.4. A thorough analysis of all measurements that conform to this observed behavior shows that they all involve polymers of MWs sufficiently high that their T_g's are virtually constant at their plateau values ($T_{g\infty}$). Under such conditions, only temperature affects the MW dependence of viscosity. As a result, isothermal measurement has become the acceptable methodology for determination of melt viscosity of traditional polymers.

Recently, increased attention has been given to low-MW polymers and oligomers, as these find more and more applications, for example, as adhesives and plasticizers. For this class of polymers, a strong dependence of free volume (and T_g) on MW causes deviations from eq. (12), when melt viscosity measurements are taken isothermally. The correct approach would be to either impose isofree volume conditions (i.e., same T_g) on the measurements, or develop alternate equations that incorporate the effect of T_g variation. This is achieved here by combining the approaches presented thus far.

A comparison of the Doolittle equation, eq. (7), and eq. (12) shows that neither A nor K' is a "constant." In actuality, A should include all dependence on MW, while K' includes temperature (and hence free volume) dependence. Thus the combination of these two equations leads to the more generalized viscosity expression:

$$\ln \eta = A' + a \ \ln M_w + \frac{b}{f} \qquad (13)$$

where

$$A = A' + a \ \ln M_w = A(M_w) \qquad (14)$$

and

$$\ln K' = \ln\left(\frac{\eta}{M_w{}^a}\right) = A' + \frac{b}{f} \qquad (15)$$

In addition, it should be noted that K' also depends on MW, because fractional free volume (f) is also a function of temperature and MW. However, if the MW is high enough, its contribution to the viscosity is negligible when $T > T_g$, and the fractional free volume might be a function of temperature alone, thus eliminating that contribution to K'.

$$K'(f(T, M_n)) = K'(f(T))|_{M_n > M_C} \qquad (16)$$

In eq. (16), the thermal dependence of the viscosity is essentially due to the friction coefficient and this coefficient also depends on the concentration of chain ends, the effect of which vanishes with increasing MW as per the isofriction analysis.[3] The temperature and MW dependence of K' in eq. (15) are already suggested in different references.[16,19] For example, η/M relationship with the temperature and MW for the empirical equation shows the K' dependence,[16,19] as suggested by eq. (15).

Finally, substituting the fractional free volume expression from eq. (9) into eq. (13) results in the generalized expression for melt viscosity:

$$\ln \eta = A' + a \ \ln M_w + \frac{b}{f_g + \alpha_f(T - T_{g\infty}) + \frac{2K}{M_n}} \qquad (17)$$

It should be noted that although eq. (17) provides a generalized viscosity equation, it is only limited for application to linear polymer systems. Nonlinear polymers,[42–54] which are also of interest to us, involve a larger number of chain ends per molecule, which affect the free volume differently. These effects, as well as the branch points effects, will be illustrated elsewhere.

RESULTS AND DISCUSSIONS

The development of a unifying approach allows the simulation and prediction of the viscosity of polymeric materials over a wide range of temperature and MW, including low-MW regions, with a simple semiempirical equation. Among many possible cases, the linear polystyrene case, a well-understood system for which extensive experimental data are available, was chosen to be simulated.

Table I presents a summary of all experimental literature studies used in this article to compare with the proposed equation. In this data set, most of the data are for narrow MW distributions ($M_w/M_n < 1.1$); hence the polydispersity effects are generally insignificant. Also, It should be noted that some of the low temperature measurements are for tensile viscosity, which is equivalent to thrice the shear viscosity.[55,61] The experimental measurements in an early study by Fox and Flory[20] do not agree with other measurements[4–7,55,56,57] at the same MW and temperature and were not used here. However, that article includes a valuable discussion about the viscosity at T_g and its dependence on MW.[20]

TABLE I
Summary of the Reference for the Viscosity Measurement

Reference	Temperature (°C)	Range of molecular weight	Technique
Majeste et al.[3]	160	$M_w = 1{,}100–2{,}700{,}000$	Zero shear viscosity (oscillatory rheometer)
Onogi[4]	160	$M_w = 5{,}000–867{,}000$	Zero shear viscosity (cylinder rheometer)
Tobolsky[55]	100	$M_w = 80{,}000–267{,}000$	Tensile viscosity (3 × shear viscosity)
Allen and Fox[5]	217	$M_v = 540–880{,}000$	Zero shear viscosity (capillary viscometer)
Fox and Flory[6,7]	217	$M_v = 4{,}900–381{,}000$	Zero shear viscosity (capillary viscometer)
Stratton[56]	183	$M_w = 48{,}000–242{,}000$	Zero shear viscosity (capillary rheometer)
Akovali[57]	129	$M_w = 82{,}000–1{,}320{,}000$	Tensile viscosity (3 × shear viscosity)
Rudd[58]	227	$M_w = 51{,}400–568{,}000$	Zero shear viscosity (capillary viscometer)
Spencer and Dillon[59]	200	$M_w = 86{,}000–710{,}000$	Zero shear viscosity (capillary viscometer)
Montfort et al.[60]	160	$M_w = 110{,}000–2{,}700{,}000$	Zero shear viscosity (oscillatory rheometer)
Plazek et al.[8]	70–180	$M_v = 1{,}100–800{,}000$	Zero shear viscosity (cylinder rheometer)
Schweizer[9]	190	$M_w = 2{,}095–2{,}700{,}000$	

The polydispersity of most of the data is less than 1.1 ($M_w/M_n < 1.1$).

TABLE II
Molecular Parameters for the Polystyrene Case

Parameter	Values	Reference
M_c	38,000	1,22,32,34,61
f_g	0.025	22,32,37
α_f (10^{-4} deg^{-1})	4.8	22,32,37
$2K/\alpha_f$	1.0×10^5	1,33
B	1	22,32,37
$T_{g\infty}$ (°C)	100	1,22,32,37
a ($M_w < M_c$)	1	22,32,37,61
a ($M_w > M_c$)	3.4	22,32,37,61

The viscosity of linear polystyrene is simulated using eq. (17). Some of the parameters for linear polystyrene can be found in the published literature[1,22,32,33,37,61]; these molecular parameters are summarized in Table II. In eq. (17), only A' is an unknown parameter to calculate the viscosity at different temperatures and MWs. Comparison to eq. (10) shows that A' can be calculated if the behavior of viscosity at T_g is known. A' will generally have two values, one at $M_w < M_c$ and another at $M_w > M_c$.

Analysis of viscosity at T_g

According to Fox and Flory,[20] the viscosity of a polymer depends not only on the mobility of each segment, but also on an intersegment cooperation factor, which increases significantly with MW. If the MW is large, viscosities well above 10^{12} P at T_g should be expected.[20] Below T_g, although the configurational structure remains unchanged as the temperature is lowered, there remains a small linear decrease in volume with temperature associated with the crystal-like "contraction of the lattice" due to decreased amplitudes of oscillation of the segments about mean fixed positions.[20]

However, the MW dependence on the viscosity at T_g is not explicitly discussed extensively in the literature. On the contrary, a lot of discussion is based on the assumption of a constant viscosity at T_g. For low-MW polymers, the viscosity at T_g was assumed to be $10^{12} - 10^{13}$ P in several literature studies.[33,42,62–64] For biomaterials also it was assumed to be around $10^{11} - 10^{12}$ P.[65–67]

More direct evidence of the MW dependence behaviors on the viscosity at T_g is presented by Tobolsky et al.,[55] who show the tensile viscosity (equivalent to thrice the shear viscosity) measurements of polystyrene at 100°C with the clear dependence of the MW with a slope of 4.0.[55] These data exhibit an experimental proof of the MW dependence on viscosity at T_g.

Since no definitive relationship for the viscosity of polystyrene at T_g can be found in the literature, we decided to extract this information from a small sub-

set of the data available. The viscosity at T_g is back calculated from eq. (10), the modified WLF equation, using four sets of literature data (Allen and Fox[5] (217 °C), Fox and Flory[6,7] (217°C), Rudd[58] (227°C), and Spencer and Dillon[59] (200°C)). These data sets were selected because they represent high temperature measurements (>200°C) with known values of T_g, T, and $\eta_o(T)$.

Figure 1 shows the data from these former studies along with a best-fit expression obtained by least squares linear regression. In obtaining this expression, the value of the critical MW for polystyrene, M_c, was fixed at 38,000, which will be used for the remainder of this study. The viscosity of polystyrene at its T_g is found to be represented by

$$\eta = 4.65 \times 10^9 \times M_w \ (P) \quad \text{for} \quad M_w < 38,000 \quad (18)$$

$$\eta = 4.74 \times 10^{-2} \times M_w^{3.4} \ (P) \quad \text{for} \quad M_w > 38,000 \quad (19)$$

The calculated and literature data agree fairly well over the entire range of molecular weight. The R^2 values for the correlation were $R^2 = 0.907$ and 0.957, below and above M_c, respectively. The T_g viscosity at the critical molecular weight, M_c, is calculated around 1.7378×10^{14} P. Combining eqs. (18) and (19), the value of A' is estimated to be -17.8269 for $M_w < M_c$ and -42.9383 for $M_w > M_c$.

Obtaining accurate knowledge of the viscosity of any given polymer at its T_g is usually the greatest obstacle to the application of the WLF equation. Now, we have this information for linear polystyrene as in eqs. (18) and (19). We can transform all the data from the literature sets of Table I to the form required by WLF. A comparison is given in Figure 2, which shows very good agreement with data sets excluded from Figure 1. This provides additional validation of eqs. (18) and (19).
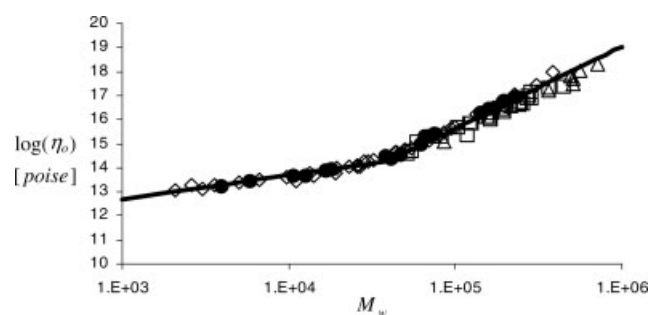

Figure 1 Viscosity of the different molecular weights of polystyrene at T_g with the different literature data using high temperature measurements (the plotted data are calculated by WLF equation and viscosity measurements). ●, 217°C – Allen and Fox[5]; ◇, 217°C – Fox and Flory[6,7] ● ● ● □, 227°C – Rudd[58]; △, 200°C – Spencer and Dillon.[59]
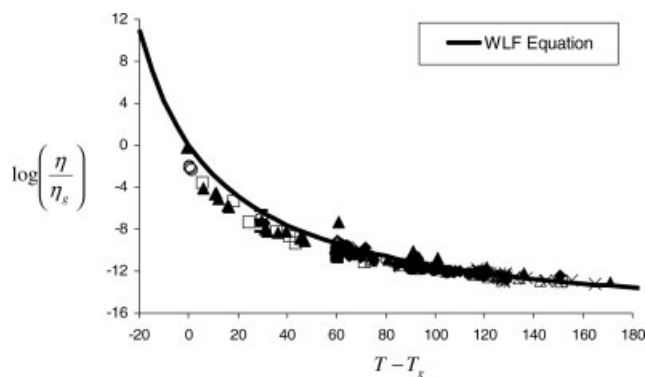
Figure 2 Results for log (η/η_g) versus $T - T_g$ of the WLF equation of polystyrene with the assumption of molecular weight dependence for the viscosity at T_g. □, this work; ◇, Onogi et al.[4]; △, Allen and Fox[5]; ×, Fox and Flory[6,7] • • •; *, Rudd[58]; –, Spencer and Dillon[59]; —, Akovali[57]; ○, Tobolsky[55]; +, Stratton[56]; ■, Montfort et al.[60]; ▲, Plazek et al.[14]; ◆, Majeste et al.[3]; ●, Schweizer.[9]

Viscosity simulation results

The simulation results for linear polystyrene viscosity at different MWs and temperatures are compared with experimental measurements in Figures 3 and 4. Various sets of data included in these figures were collected in our laboratory using the RMS-800 (Rheometrics, Inc.). Figure 3 presents the simulation results for linear polystyrene at 160°C along with all experimental data found for this temperature. It is evident that, even though the parameters are estimated from high temperature measurements (>200°C), the unifying equation is capable of predicting the viscosity behavior at lower temperature (160°C) in both regions: $M_w < M_c$ and $M_w > M_c$. Figure 3 clearly
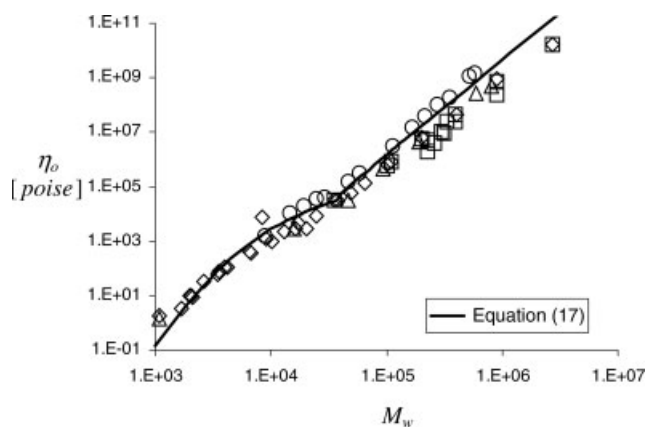

Figure 3 The Comparison of the calculation by eq. (17) and experimental measurement from the literatures of linear polystyrene viscosity behavior versus molecular weight at 160°C. ○, 160°C – Onogi et al.[4]; ◇, 160°C – Majeste et al.[3]; □, 160°C – Montfort et al.[60]; △, 160°C – Plazek et al.[14]

shows the curvature behavior below M_c, which is characteristic of isothermal measurements. The linear dependence of viscosity on MW below M_c is only exhibited when isofree volume conditions are maintained, as, for example, in Figure 1 at T_g.

Figure 4 presents the simulated results over a wide range of temperature and molecular weight as compared to a considerable corpus of experimental data. Of noted significance is the fact that the prediction of viscosity in Figure 4 covers a wide range of MW and temperature with only one estimated parameter.

The viscosity predicted at low temperatures, ca. 100, 110, and 129°C, and high MW is somewhat higher than the experimental values. The data at 100°C and 129°C are indirect measurements from tensile viscosity. This could be the reason why some of these measurements deviate from the simulation results at high-MW and low-temperature regions. However, most of the high temperature measurements agree with the calculations remarkably well. Figure 5 illustrates the temperature effect on the viscosity behavior of the lin-
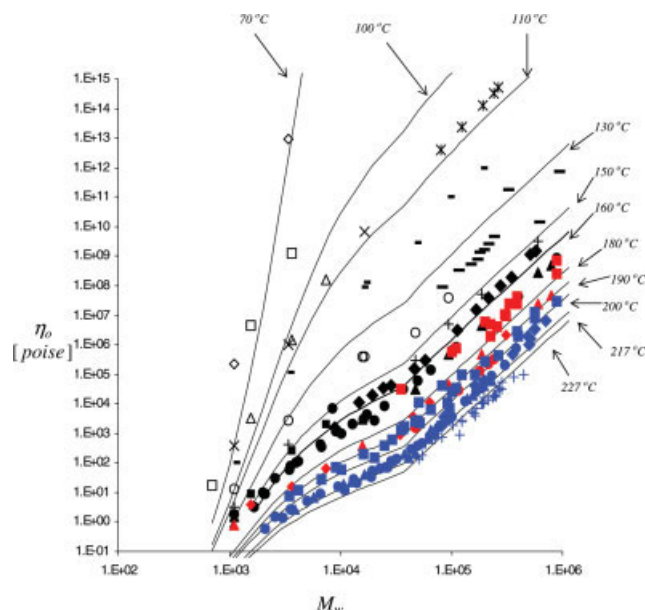

Figure 4 The comparison of the calculation eq. (17) and experimental measurement from the literature of linear polystyrene viscosity behavior versus molecular weight with different temperatures. □, 70°C – this work; ◇, 70°C – Plazek et al.[14]; △, 100°C – this work; ×, 100°C – Plazek et al.[14]; *, 100°C – Tobolsky[55]; –, 110°C – Plazek et al.[14]; –, 129°C – Akovali[57]; ○, 130°C – Plazek et al.[14]; +, 145°C – Plazek et al.[14]; ■, 150°C – this work; ◆, 160°C – Onogi et al.[4]; ▲, 160°C – Plazek et al.[14]; ●, 160°C – Majeste et al.[3]; ■, 160°C – Montfort et al.[60]; ◆, 180°C – this work; ▲, 180°C – Plazek et al.[14]; ●, 183°C – Stratton[56]; ■, 190°C – Schweizer[9]; ◆, 200°C – Spencer and Dillon[59]; ▲, 217°C – Allen and Fox[5]; ●, 217°C – Fox and Flory[6,7] • • •; +, 227°C – Rudd.[58] [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
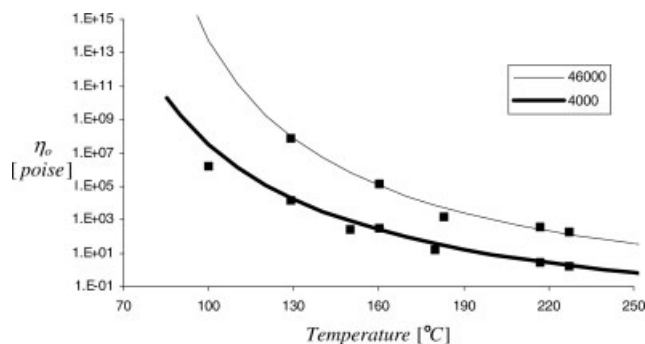
Figure 5 Comparison of the melt viscosity versus temperature of polystyrene with the different molecular weight from the calculation eq. (17) and experimental data.

ear polymer. The experimental data in Figure 5 were collected from literature and came from the list in Table I. Here, the MW is selected specifically in both regions: 4000 ($<M_c$) and 46,000 ($>M_c$). The simulation results in Figure 5 were calculated using eq. (17) by fixing the value of MW to these respective values. Excellent agreement is seen between experimental and simulated results.

While the approach presented here is demonstrated to allow the accurate prediction of viscosity over a wide range of temperature and molecular weight, the representation of eq. (17) loses the elegance generally associated with viscosity versus MW plots. Stemming from familiarity with solution viscosity measurements, in which the solution T_g is minimally affected by MW, researchers have come to expect figures showing M_w^1 and $M_w^{3.4}$ dependence below and above M_c, respectively.

It is now clear that the deviation from this familiar picture at low MW is rooted in the shape of the dependence of T_g on MW. However, this effect can be eliminated if the experimental measurement technique is modified such that measurements are carried out under isofree volume conditions, i.e., a constant ($T - T_g$), given by eq. (2), rather than isothermal conditions. Under such conditions, eq. (17) can be rewritten as

$$\eta = K'M_w^a \qquad (20)$$

where K' is given by $e^{A'+b/f}$, which is obviously constant for a constant value of the free volume f. In Figure 6, two such sets of data were collected by selection from the data corpus of Table I. For the first set ($T - T_g$) is fixed at 60°C, while it is set to 117°C for the second set. Molecular weight effects on T_g have been factored into this selection. The data compare remarkably well to the calculated viscosity curves obtained form eq. (20) at the respective $T - T_g$ values. The resulting correlations are

$$\eta = \begin{cases} 2.13 \times M_w & (M_w < M_c) \\ 2.65 \times 10^{-11} \times M_w^{3.4} & (M_w > M_c) \end{cases} \text{ at } T - T_g = 60°C$$

and

$$\eta = \begin{cases} 4.06 \times 10^4 \times M_w & (M_w < M_c) \\ 5.04 \times 10^{-14} \times M_w^{3.4} & (M_w > M_c) \end{cases} \text{ at } T - T_g = 117°C$$

The effect of ($T - T_g$) also reflects another class of universality as can be seen from the rearrangement of eq. (17) as

$$\ln\frac{\eta}{M_w^a} = A' + \frac{b}{f_g + \alpha_f(T - T_g)} \qquad (21)$$

$$(i) \ M < M_c : \ln\frac{\eta}{M_w} = A'_1 + \frac{b}{f_g + \alpha_f(T - T_g)} \qquad (22)$$

$$(ii) \ M > M_c : \ln\frac{\eta}{M_w^{3.4}} = A'_2 + \frac{b}{f_g + \alpha_f(T - T_g)} \qquad (23)$$

This suggests a universal relation between η/M_w^a and $T - T_g$ as plotted in Figure 7, which also shows remarkable agreement with data.

Analysis of shift factor

Another useful tool that is often used in analyzing rheology data is the so-called temperature shifting factor. It is based on the observation that material functions, including rheological properties, have a strong correlation with temperature and have similar temperature dependence curves. This similarity provides the basis for an important empirical method,
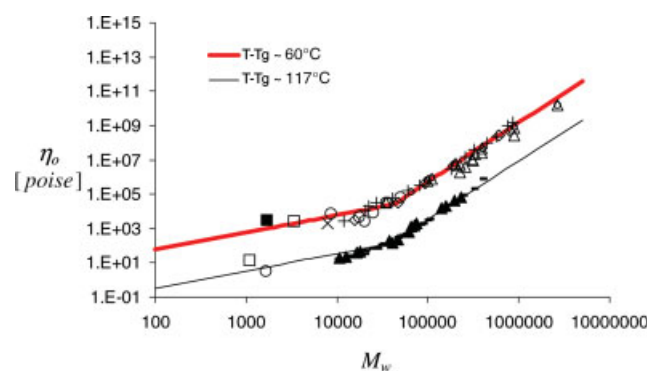

Figure 6 Comparison of the simulated and experimental data of polystyrene for the iso-free volume conditions ($T - T_g = 60$ and 117°C) with the different molecular weights. ■, 100°C – this work; □, 130°C – Plazek et al.[14]; ×, 150°C – this work; ◇, 160°C – Plazek et al.[14]; △, 160°C – Montfort et al.[60]; ○, 160°C – Majeste et al.[3]; +, 160°C – Onogi et al.[4]; –, 217°C – Fox and Flory[6,7] • • •; ▲, 217°C – Allen and Fox.[5] [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
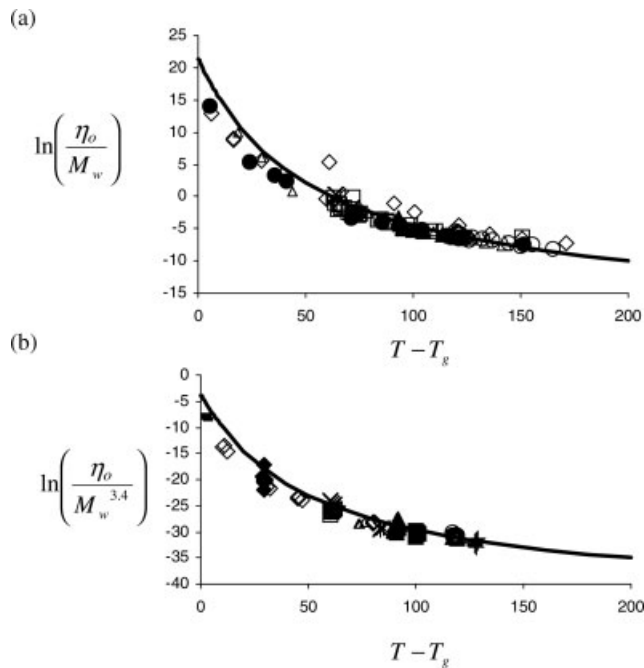
(a)

(b)

Figure 7 Results for $\ln(\eta/M_w^a$ versus $T - T_g$ with the calculation eq. (21) and different experimental data of polystyrene from literature. (a) $M_w < M_c$ and $a = 1$; (b) $M_w > M_c$ and $a = 3.4$. ●, this work; ×, Onogi et al.[4]; ○, Allen and Fox[5]; △, Fox and Flory[6,7] ● ● ●; ◇, Plazek et al.[14]; □, Majeste et al.[3]; ▲, Schweizer[9]; +, Rudd[58]; ◆, Akovali[57]; –, Tobolsky[55]; *, Stratton[56]; —, Montfort et al.[60]; ■, Spencer and Dillon.[59]

known as the "method of reduced variables," for combining data taken at several different temperatures into one master curve.[61] Because of these characteristics, the study of shifting factor has become an important aspect of rheological studies. Usually, the temperature shifting factor is used to obtain a master curve for the viscosity function at an arbitrary reference temperature yet at a fixed MW. The temperature-shifting factor (α_T), in terms of viscosity, is defined as

$$\alpha_T = \frac{\eta(T)T_r\rho_r}{\eta(T_r)T\rho} \quad (24)$$

where η is zero shear viscosity, and ρ and ρ_r are the density at T and T_r respectively. Using this definition and the WLF equation, we can derive an expression for α_T. Without loss of generality, we can assume that the ratio $(T_r(\rho)_r/T(\rho))$ is unity since it is very close to that value under most practical conditions.[61]

$$\ln \alpha_T = \frac{(\frac{b}{f_{r\infty}})(T - T_r)}{(\frac{f_{r\infty}}{\alpha_f}) + (T - T_r)} \quad (25)$$

The temperature-shifting factor of eq. (25) has been demonstrated to work well for polymers of high

MW. However, as in this case of viscosity measurements studies indicate the limitation of using this technique when either large differences in MW exist, or the MWs involved are low enough (e.g., $M_w < M_c$).[2,4,22] These limitations are illustrated by the necessity of using $f_{r\infty}$ in eq. (25), where $f_{r\infty}$ is the free volume at the reference temperature, T_r, and a MW high enough, $M_w > M_c$. At such MWs, the free volume dependence on MW becomes negligible. This is clear from Figure 8, which represents a plot of $f_r(M_n)$, the free volume at a given reference temperature, T_r, versus MW as given by

$$f_r(M_n) = f_g + \alpha_f(T_r - T_{g\infty}) + \frac{2K}{M_n} = f_{r\infty} + \frac{2K}{M_n} \quad (26)$$

For a more generalized shifting factor, which considers the shift of the material property from reference temperature, number–average molecular weight, and weight–average molecular weight (T_r, M_{nr}, and M_{wr}) to any temperature, number–average molecular weight, and weight–average molecular weight (T, M_n, and M_w), the definition of eq. (24) is expanded and combined with eq. (17) to provide

$$\ln \alpha_{T,M} = (A' - A_r') - \ln\left(\frac{M_{wr}^a}{M_w^a}\right)$$

$$- \frac{b}{f \times f_r}\left[\alpha_f(T - T_r) + 2K\left(\frac{1}{M_n} - \frac{1}{M_{nr}}\right)\right] \quad (27)$$

where f is at T and M_n and f_r is at T_r and M_{nr}. A' and A_r' are the constants for the case of M_w and M_{wr}, which are already evaluated in eq. (17) for the below and above M_c. Also, depending on M_w and M_{wr}, a and a_r can be determined as the value of 1 or 3.4 for below or above M_c, respectively. Obviously, if the molecular weight distribution is kept constant, i.e.,
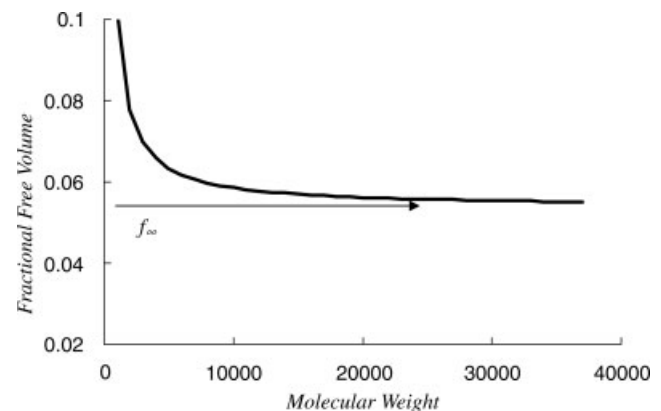

Figure 8 Fractional free volume behavior calculation depending on the molecular weight of polystyrene at 160°C using eq. (26) with parameters in Table II.
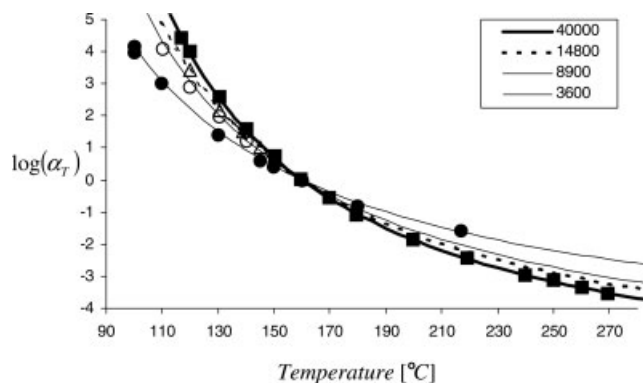
Figure 9 Temperature dependence calculations of the temperature shifting factor (α_T) with the different molecular weights (M_w) of polystyrene. ■, Onogi et al.[4] – $M > M_c$; △, Onogi et al.[4] – 14,800; ○, Onogi et al.[4] – 8900; ●: this work, Allen and Fox,[5] Fox and Flory,[6,7] ● ● ● Majeste et al.,[3] and Plazek et al.[14] (3400–4000).

Figure 10 Comparison of calculation and experimental data of the linear plots of $-(T - T_r)/\log \alpha_T$ versus $T - T_r$ for the linear polystyrene with different molecular weights (M_w). ■, Onogi et al.[4] – $M \gg M_c$; △, Onogi et al.[4] – 14,800; ○, Onogi et al.[4] – 8900; ●: this work, Allen and Fox, et al.[5] Fox and Flory,[6,7] ● ● ● Majeste et al.,[3] and Plazek et al.[14] (3400–4000).

$M_w = M_{wr}$ (and $M_n = M_{nr}$), eq. (27) can be reduced to the simpler form

$$\ln \alpha_T = -\frac{b}{f(M_{nr}, T) \times f_r(M_{nr})} [\alpha_f (T - T_r)] \qquad (28)$$

which can be rewritten, after substituting the expression of f with M_{nr} and T, as

$$\ln \alpha_T = \frac{\left(\frac{b}{f_r}\right)(T - T_r)}{\left(\frac{f_r}{\alpha_T}\right) + (T - T_r)} \qquad (29)$$

While this equation appears similar to the expression traditionally used for α_T, as in eq. (25), the latter is only a special case of the general eq. (28). That limit is attained as M_n is large enough ($>M_c$) and f_r tends to its limiting value $f_{r\infty}$.

These phenomena have been noted by Onogi et al.,[4] who measured the viscosity of polystyrene at a reference temperature of 160°C and various molecular weights. Their data are compared with eq. (28) in Figure 9, which clearly demonstrates the effect of MW on the shifting factor. Figure 9 also shows the saturation behavior, above M_c, which is represented by the thick solid curve. This can also be expressed, using the linearized form, as

$$\frac{T - T_r}{\log \alpha_T} = -\frac{2.303 f_r}{b} \left[\frac{f_r}{\alpha_f} + (T - T_r)\right] \qquad (30)$$

A clear representation is provided in Figure 10 using this linearized form, eq. (30), which further confirms the trends.

On the other hand, eq. (27) allows for a different type of shifting where temperature is kept constant
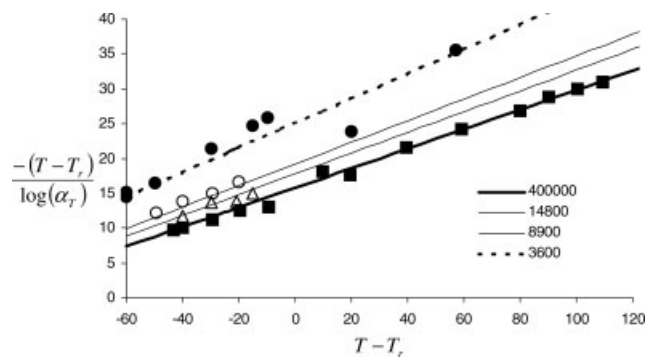
and prediction of material properties versus molecular weight is undertaken. For these conditions,

$$\ln \alpha_M = (A' - A'_r) - \ln\left(\frac{M_{wr}^a}{M_w^a}\right)$$
$$- \frac{b \times 2K}{f(M_n, T_r) \times f_r(M_n)} \left(\frac{1}{M_n} - \frac{1}{M_{nr}}\right) \qquad (31)$$

The case of 160°C is plotted for α_M using the different values (38,000 (M_c), 1000, 1,000,000) of M_{wr} (and M_{nr}) with eq. (31), in Figure 11. Same sets of data are used for the different M_{wr} (and M_{nr}) calculations. Note that the calculations and experiments reflect the same information of the MW dependence with the different scales as clear from the equations.
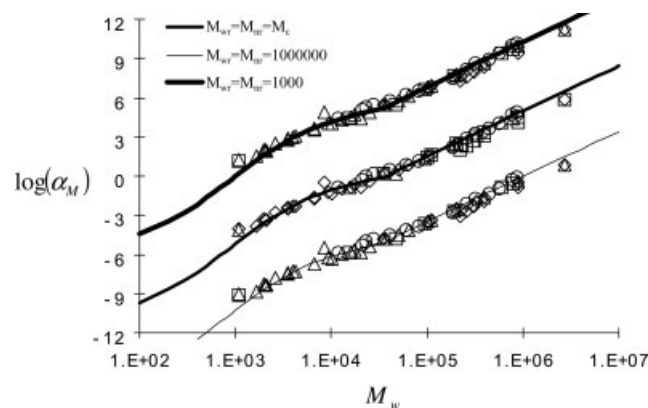

Figure 11 Molecular weight dependence of the molecular weight shifting factor (α_M) of polystyrene with the different reference molecular weights (M_{wr} and M_{nr}) at 160°C. ○, 160°C – Onogi et al.[4]; ◇, 160°C – Majeste et al.[3]; □, 160°C – Montfort et al[60]; △, 160°C – Plazek et al.[14]

CONCLUSIONS

The utility of free volume theory to the understanding of the thermal and rheological behaviors of polymers is demonstrated. Understanding and expanding the free volume concept to the different MW and temperature effects leads to the development of a semiempirical expression for melt viscosity. This is based on the generalized-unifying free volume approach considering several physical effects on the fractional free volume in linear polymeric materials. Those equations are developed and compared with the published literature and experimental data. Even though the equation is semiempirical, the agreement between the calculations and experimental data shows a clear picture of several effects on the physical behaviors of the linear polymers.

Using this approach, we were able to make the following conclusions:

1. The viscosity at T_g is a function of MW which exhibits the expected power dependence of 1 and 3.4, below and above M_c, respectively. A correction for polystyrene was extracted from a limited literature data set and presented.
2. Isothermal melt viscosity measurements can be fully described by a semiempirical universal equation, but exhibit curvature in the low-MW regions. Data for polystyrene confirm this effect.
3. Measurements at isofree volume exhibit linearity of viscosity versus MW in low MW ranges (on a log–log scale).
4. Shifting factors can be derived using the same approach and are seen to also depend on MW.

The linear polystyrene system was selected in this study for the large corpus of literature data and experimental measurements available. However, this approach is applicable to other polymer systems and should be tested on a variety of linear polymers in the future. In a preliminary analysis of other materials, such as polybutadiene and polyisobutylene, we have found similar types of effects but were limited by the dearth of usable literature data for these systems and thus these studies remain inconclusive. However, this demonstrates the potential for the expansion of this approach to a scope covering other polymers, copolymers, and/or polymer blends. Such analyses would be of great value for the development of novel industrial applications such as low VOC and high solids coating formulations.

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