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Zero-Shear Viscosity Exponent and Polydispersity Effects

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ABSTRACT: The zero-shear viscosity of linear chain high polymer melts in the entanglement region is related to the molecular weight by the empirical relation $\eta \propto M^a$, with the widely quoted viscosity exponent $a = 3.4$. The molecular origin of this power law dependence, in particular the value of a, is a topic of considerable interest since it appears to be a basic property of these viscoelastic systems. The reptation model of de Gennes predicts an exponent $a = 3$, and although intriguing theoretical explanations of the discrepancy with experiment have been proposed by other workers, none is completely satisfactory. A resolution of this problem is important because it seriously questions the correctness of the fundamental reptation model. A new explanation recently put forth in an attempt to resolve this issue in favor of reptation theory is that polydispersity effects can account for the deviation when M is replaced by $M^* \equiv (M_wM_zM_{z+1})^{1/3}$. In this paper we have examined this claim for a variety of polydisperse systems and have found it to be completely unjustified. General considerations show that in systems for which the *rate of change* of polydispersity with molecular weight is sufficiently high, substantial changes in the viscosity–molecular weight relation must occur when reexpressed in terms of different average molecular weights, and only one kind of average molecular weight can provide a viscosity exponent which is constant. Existing data show that log η is linear against log M_w, but certainly not against log M_v, log M_n, log M_z, or log M^*. This result is complemented by our analysis of studies of anionically polymerized systems, for which extensive data support an exponent $a = 3.4$. Due to the very small rate of variation of polydispersity in these systems, there are no significant corrections to the viscosity exponent as a result of adjusting it to any preferred type of average molecular weight such as M^*. Thus the discrepancy in the value of the viscosity exponent remains. Although it may have other causes, it cannot be explained by polydispersity effects through modification of the choice of average molecular weight.

1. Introduction

Molecular theories developed recently for the rheology of linear chain high polymer melts give different microscopic interpretations of the empirical relation[1]

$$\eta \propto M^a \tag{1.1}$$

between the zero-shear viscosity η and the molecular weight M, with the widely quoted value $a = 3.4$ for the entanglement regime. The reptation model,[2] while very appealing, predicts $a = 3$. Several explanations have been advanced to explain this discrepancy. For example, Doi[3] considers the effect of length fluctuations on chain diffusion and obtains a correction to this value. However, he finds that the power law form of eq 1.1 is not strictly obeyed and that the local zero-shear viscosity exponent

$$a(M) \equiv \partial \ln \eta / \partial \ln M \tag{1.2}$$

is not a constant but depends on M, which disagrees with experiment. From a different vantage point Curtiss and Bird[4] find that their phase–space kinetic theory allows $a = 3 + \beta$ with $\beta > 0$. An exponent differing from 3 can also be obtained within the context of reptation theory by considering a model of hindered reptational diffusion.[5] Unfortunately, these two approaches do not give actual values for the exponent. A different explanation has been proposed[8,9] which suggests that polydispersity effects can account for the deviation between the empirical exponent and the value predicted by reptation theory, but this claim has not been analyzed in detail. Thus the nature of the discrepancy in the viscosity exponent between empirical data and the reptation model remains an open question.

In this paper we address the effects of polydispersity on the molecular weight dependence of the zero-shear viscosity. In fact, there are no data for truly monodisperse samples and most systems must be characterized by some type of average molecular weight $\bar{M}$. One can then attempt to fit a power law of the form in eq 1.1 with M replaced by $\bar{M}$:

$$\eta \propto \bar{M}^a \tag{1.3}$$

However, one must recognize that the value of the zero-shear viscosity exponent a and, more generally, the form of the viscosity–molecular weight relation itself, will usually depend on the type of average molecular weight with which the viscosity is correlated.

In an analysis of polydisperse reptating melt systems Daoud and de Gennes[6] have stated that the viscosity should be proportional to the weight average of the relaxation time provided by reptation theory for monodisperse systems. This relaxation time varies as the cube of the molecular weight. Computing this average, one finds[7]

$$\eta \propto (M^*)^3 \tag{1.4}$$

where the average molecular weight to be used is

$$M^* \equiv (M_wM_zM_{z+1})^{1/3} \tag{1.5}$$

It was recently suggested[8,9] that observed values of the zero-shear viscosity exponent differ from the value $a = 3$

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because they are based on measurements performed in polydisperse systems and because they rely on correlations of the viscosity with incorrect choices of average molecular weight. By using M^* it was stated that one would in fact verify eq 1.4 in any linear chain melt system, thereby vindicating reptation theory.

We have examined this claim for two classes of polydisperse systems that have been studied in the literature and have found it to be unjustified.

For systems possessing narrow unimodal molecular weight distributions obtained through anionic polymerization, our quantitative analysis of representative data shows that the empirical viscosity exponent is insensitive to changes in the type of average molecular weight used. The polydispersity in such systems is so nearly constant that the separation between the different average molecular weights of interest has negligible variation. Consequently, any choice among these average molecular weights will determine the viscosity exponent. As we show below, this value exceeds 3 in most studies of polystyrene.

We have also considered studies of truly polydisperse systems, those which allow one to discriminate between different definitions of average molecular weight. One example is provided by polymer blends having well-separated bimodal molecular weight distributions. In these systems most average molecular weights will vary so widely from one another that only a few can be consistent with a linear log η–log M relation. We have found that the average molecular weight M^* defined by eq 1.5 completely fails to give a power law.

Empirically, the widely quoted value $a = 3.4$ for the entanglement regime is supported by viscoelastic data on a variety of linear homopolymers, as collected in the early review by Berry and Fox.[10] The individual case of anionically polymerized polystyrene has been studied the most and has yielded a large set of data from independent laboratories. The review by Casale et al.[11] tabulates values of a from 3 to 3.5 derived from 15 of the apparently more reliable investigations of polystyrene. These values cluster near 3.4 but their scatter is a source of concern. Since one believes that a given chemical species of polymer will exhibit, under monodisperse conditions, a definite viscosity–molecular weight dependence, it is also important to check the reliability of experimental data and to determine the influence of systematic errors. For one fixed series of narrow-distribution polystyrenes, we observe that closer extrapolation to zero shear[12,13] changes a by 0.1 and elimination of one data point produces a deviation of 0.2, while different determinations[13,14] of M modify a by 0.2. Such effects are no doubt responsible for some of the scatter between the other polystyrene studies referred to above. However, in this report our attention is focused solely on the possible effects of polydispersity.

2. General Analysis

In this paper we examine the possible effects of polydispersity on the molecular weight dependence of the zero-shear viscosity by using model molecular weight distributions. Model distributions allow us to calculate any type of average molecular weight in a set of polymer samples and thereby enable us to predict the dependence of viscosity–molecular weight relations on the choice of average molecular weight for different conditions of polydispersity.

The degree of sensitivity of the viscosity–molecular weight relation to the choice of average molecular weight (AMW) is certainly affected by the polydispersity itself, but it is mainly dependent on the amount of variation in polydispersity. For example, we consider what can happen when there is no change in polydispersity, as in a set of polymers where each sample has the same form of molecular weight distribution (MWD) with a polydispersity that is independent of molecular weight. In this case the ratio $\bar{M}/\bar{M}'$ of any two particular average molecular weights $\bar{M}$ and $\bar{M}'$ will be a constant independent of the molecular weight of the sample. Consequently, if the power law in eq 1.3 holds for one type of AMW, it will also hold, with the same constant exponent, for any other choice of AMW.

Thus the key ingredient in an analysis of polydispersity effects is the *rate of variation* in polydispersity. In this section we gauge the influence of this factor by considering a hypothetical set of samples having known molecular weight distributions, in the form of a smoothly varying one-parameter family. We relate the changes in a given viscosity–molecular weight relation, when it is expressed in terms of different average molecular weights, to the way in which the polydispersity varies from sample to sample.

We assume that the molecular weight distribution of each sample is uniquely determined by the molecular weight. This implies a relation $\bar{M}'(\bar{M})$ between any two AMWs throughout the set of samples and allows us to transform a viscosity–molecular weight relation $\eta(\bar{M})$, given in terms of the average molecular weight $\bar{M}$, into the relation $\eta(\bar{M}')$ corresponding to $\bar{M}'$ by change of variables. When the properties of the samples change continuously with molecular weight, we can also work with the local viscosity exponent $a(\bar{M})$ defined in eq 1.2. Its functional form depends on the choice of average molecular weight as well and transforms according to

$$\frac{a(\bar{M}')}{a(\bar{M})} = \frac{\partial \ln \bar{M}}{\partial \ln \bar{M}'} = \left\{1 + \frac{\partial \ln (\bar{M}'/\bar{M})}{\partial \ln \bar{M}}\right\}^{-1} \quad (2.1)$$

In the following development we deal with the viscosity exponent instead of the viscosity.

To represent the molecular weight distributions we assume that their form is fixed throughout the set of samples. This is a reasonable simplification since most measurements deal with samples that have each been polymerized under mutually similar conditions. The change in polydispersity can then be expressed in terms of the parameters which apply to that form of MWD. If we use a two-parameter family $\{\bar{M},P\}$ of model distributions, we can convert it into a one-parameter family by supposing a smooth relation $P(\bar{M})$ between the polydispersity measure

$$P \equiv M_w/M_n \quad (2.2)$$

and some average molecular weight $\bar{M}$. In eq 2.2 M_w is the weight-average molecular weight while M_n is the number-average molecular weight. (Definitions of these are recalled in Appendix B.) Equation 2.1 can then be rewritten

$$\frac{a(\bar{M}')}{a(\bar{M})} = \left\{1 + \frac{\partial \ln (\bar{M}'/\bar{M})}{\partial \ln P}\,\frac{\partial \ln P}{\partial \ln \bar{M}}\right\}^{-1} \quad (2.3)$$

This version directly relates the viscosity exponent shift to the *rate* of polydispersity variation $\partial \ln P/\partial \ln \bar{M}$ and to the function

$$S_{\bar{M}',\bar{M}}(P) \equiv \partial \ln (\bar{M}'/\bar{M})/\partial \ln P \quad (2.4)$$

The latter quantity measures the rate of separation of the two molecular weight averages with changing polydispersity.

Equation 2.3 makes it clear that regardless of the degree of polydispersity, there is no shift in the viscosity exponent

Table I
Ratios of Average Molecular Weights in Terms of the Polydispersity $P \equiv M_w/M_n$ for Log-Normal and Schulz Model Distributions[15]

model MWD	M^*/M_w	M_v/M_w
log-normal	P	$P^{(q-1)/2}$
Schulz	$\left\{\frac{(3P-2)(2P-1)}{P^2}\right\}^{1/3}$	$\frac{P-1}{P}\left\{\frac{\Gamma(q+P/(P-1))}{\Gamma(P/(P-1))}\right\}^{1/q}$

when the polydispersity is independent of molecular weight. A convenient indicator of the kind of polydispersity variation $P(\bar{M})$ needed to change the viscosity exponent by various amounts is obtained by considering eq 2.3 for a constant ratio of exponents. We then find the first-order differential equation

$$\partial \ln P/\partial \ln \bar{M} = c_{\bar{M}',\bar{M}}/S_{\bar{M}',\bar{M}}(P) \qquad (2.5)$$

for $P(\bar{M})$, where

$$c_{\bar{M}',\bar{M}} \equiv -1 + a(\bar{M})/a(\bar{M}') \qquad (2.6)$$

is an adjustable constant.

Existing studies usually compare the viscosity with M_w or M_v, the latter being the viscosity-average molecular weight. (M_v is defined in Appendix C and shown to be less than M_w.) However, as remarked in the Introduction, it is also of considerable interest to examine the dependence of the viscosity on the average molecular weight M^*. Thus we consider eq 2.5 when the choice of average molecular weight changes from $\bar{M} = M_w$ to $\bar{M}' = M_v$ or $\bar{M}' = M^*$.

The form of eq 2.5 depends on the term $S_{\bar{M}',\bar{M}}(P)$, which in turn depends on the MWD. Two well-known distributions that are often used to represent real polymers with unimodal MWDs are the log-normal and Schulz two-parameter models.[15] Table I gives the ratios M_v/M_w and M^*/M_w as functions of the polydispersity P for each of these model distributions. For the log-normal distribution we then use eq 2.4 to obtain the simple results

$$S_{M^*,M_w}(P) = 1 \qquad (2.7)$$

and

$$S_{M_v,M_w}(P) = (q-1)/2 \qquad (2.8)$$

where q enters via the definition of M_v. Thus in the special case of a log-normal distribution, both expressions are independent of P. This implies that constant exponent ratios $a(M^*)/a(M_w)$ and $a(M_v)/a(M_w)$ can be simultaneously produced by a single polydispersity relation $P(\bar{M})$. Replacing the right-hand side of eq 2.5 by a single constant c, we integrate and immediately find this relation to be

$$P(M_w) \propto M_w^{\ c} \qquad (2.9)$$

The constant exponent ratios consistent with this polydispersity variation are then found from eq 2.6–2.8. They are

$$a(M^*)/a(M_w) = 1/(1+c) \qquad (2.10)$$

and

$$a(M_v)/a(M_w) = 1/(1-c/4) \qquad (2.11)$$

In eq 2.11, and in the remainder of this paper, we have specialized to the case where the viscosity-average molecular weight is defined with $q = 0.5$. (It is then relevant to cases where empirical M_v values are determined by intrinsic viscosity measurements in Θ solvents.) The corresponding results for the Schulz distribution do not simplify to the same extent due to the more complicated form of the molecular weight ratios in Table I, but they are qualitatively similar.

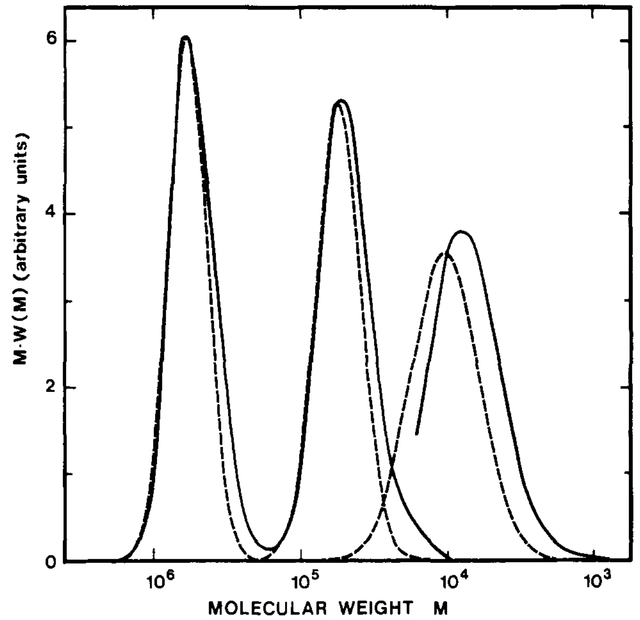

Figure 1. Typical molecular weight distributions for anionic polystyrenes. Solid curves: GPC data of Onogi et al.[16] Dashed curves: log-normal model fitted to the data. $W(M) \propto M{\cdot}N(M)$, where $N(M)$ is the number distribution.

Although they refer to the simple case of a constant shift in the viscosity exponent, eq 2.10 and 2.11 together with eq 2.9 suggest the general manner in which the variation of polydispersity with molecular weight can be expected to determine the change in the viscosity–molecular weight relation $\eta(M_w)$ when reexpressed in terms of M_v or M^*. When the polydispersity increases with molecular weight, we expect the exponents to obey the inequality $a(M_v) > a(M_w) > a(M^*)$. When it decreases, we expect $a(M_v) < a(M_w) < a(M^*)$. In the following sections we use the above analysis to guide our interpretation of polydispersity effects in polymer melt systems that have been measured by other workers.

3. Anionically Polymerized Polystyrene

The magnitude of polydispersity effects for anionically polymerized systems is an important question since highly regarded studies of the dependence of the zero-shear viscosity on molecular weight have been made for melts of such polymers. In particular, we consider the work of Onogi et al.,[16] which gives a constant value $a(M_w) = 3.7$ derived from eight polystyrene samples ranging in M_w from 59 000 to 616 000. Fortunately, actual MWD curves obtained from gel permeation chromatography are provided in a second paper,[17] and using their M_w and M_n values, we were able to obtain a reasonable fit with a log-normal MWD. Figure 1 illustrates this fit for three of the samples. Due to the small width of these distributions, a Schulz MWD gave similar agreement.

We note that the quoted polydispersity values $P \equiv M_w/M_n$ show a decrease with increasing molecular weight, which is not surprising since ideal anionic polymerization would show a sharp decrease. Since this suggests inserting a negative exponent c in eq 2.10 and 2.11, it leads us to

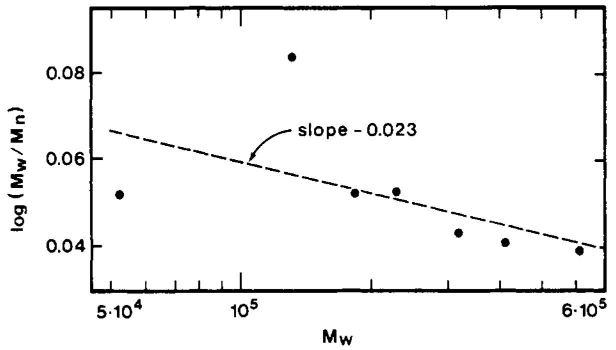

Figure 2. Variation of polydispersity $P \equiv M_w/M_n$ with weight-average molecular weight M_w for high molecular weight anionic polystyrenes studied by Onogi et al.[16] Dashed curve: least-squares fit $P \propto M_w^{-0.023}$.

expect $a(M_v) < a(M_w) < a(M^*)$. To examine this in more detail, we plot log P against log M_w in Figure 2 for those polystyrene samples lying in the entanglement region $\bar{M} > M_c$, where M_c is a critical molecular weight. According to the analysis of the previous section, a smooth variation $P \propto M_w^c$ would lead to constant shifts in the viscosity exponents, given a log-normal shape for the molecular weight distributions. If we fit this to the data, we obtain a least-squares slope $c = -0.023$. The quality of fit is certainly satisfactory for our purposes. Equations 2.10 and 2.11 then give

$$a(M^*)/a(M_w) = 1.024 \qquad (3.1)$$

and

$$a(M_v)/a(M_w) = 0.994 \qquad (3.2)$$

Evidently, the expected shift in the viscosity exponent when $M_w \to M^*$ or $M_w \to M_v$ is quite negligible for this experiment.

To check the sensitivity of the above test to the model molecular weight distribution, we compare the viscosity exponent shifts predicted in eq 3.1 and 3.2 from the log-normal distribution with those predicted with the Schulz model. Since the Schulz MWD does not yield as simple a prediction for $P(M_w)$ as given in eq 2.9 for the log-normal model, we prefer an alternate analysis based directly on the ability to compute M^* and M_v given the form of MWD. We assume that the viscosity–molecular weight relation is approximately a power law for each type of average molecular weight $\bar{M}$, with a fixed exponent $\langle a_{\bar{M}} \rangle$ determined by the slope in a linear least-squares fit to a set of data $\{\ln {}^i\bar{M}, \ln {}^i\eta\rangle_{i=1...N}$. We then consider the new slope $\langle a_{\bar{M}'} \rangle$ that would be obtained by another least-squares fit to the modified set of data $\{\ln {}^i\bar{M}', \ln {}^i\eta\}_{i=1...N}$. Employing the analysis of Appendix A, we find that the ratio of the new and old slopes can be well estimated solely in terms of the initial and final molecular weights by the formula

$$\frac{\langle a_{\bar{M}'} \rangle}{\langle a_{\bar{M}} \rangle} \simeq \frac{N \sum_i \ln {}^i\bar{M} \ln {}^i\bar{M}' - \sum_i \ln {}^i\bar{M} \sum_i \ln {}^i\bar{M}'}{N \sum_i \ln {}^i\bar{M} \ln {}^i\bar{M} - \sum_i \ln {}^i\bar{M} \sum_i \ln {}^i\bar{M}} \qquad (3.3)$$

where $\sum_i = N$. Upon using both log-normal and Schulz MWDs to compute M_v and M^* for those polystyrene samples of Onogi et al. lying in the entanglement region $\bar{M} > M_c$, we put $\bar{M} = M_w$ and $\bar{M}' = M_v$ or $\bar{M}' = M^*$ to obtain the deviations stated in Table II. It is reassuring that the exponent shifts suggested by this method for the log-normal distribution are in close agreement with those predicted in eq 3.1 and 3.2 and based on the alternate analysis of section 2. Comparing these with the shifts for the Schulz distribution, we see that the effect of changing the molecular weight distribution is not serious.

Table II
Shifts in Least-Squares Viscosity Exponent When $M_w \to M_v$ and $M_w \to M^*$ for Narrow-Distribution Polystyrenes Studied by Onogi et al.[16]

model MWD	$\langle a_{M^*} \rangle / \langle a_{M_w} \rangle$	$\langle a_{M_v} \rangle / \langle a_{M_w} \rangle$
log-normal	1.023	0.994
Schulz	1.017	0.995

It is clear that in the data of Onogi et al. there are no experimentally significant corrections to the viscosity exponent a_{M_w} when reevaluated for other AMWs such as M_v and M^*. This is due to the low rate of variation of polydispersity with molecular weight. Furthermore, when the polydispersity decreases with increasing molecular weight, as would be expected for anionically polymerized systems in general, one has $a(M^*) > a(M_w)$. As summarized in the Introduction, other studies of low-polydispersity polystyrene melts have been made, and each tends to give a value for the zero-shear viscosity exponent a_{M_w} that exceeds 3. Thus the exponent $a(M^*)$, if it changes at all, ought to deviate even further from the value 3.

Since the result of our quantitative analysis of the data of Onogi et al. is generally applicable to any study of anionically polymerized samples, we conclude that in such systems polydispersity corrections by themselves cannot explain the deviation of the zero-shear viscosity exponent from the prediction of 3 made by reptation theory. The low rate of variation of polydispersity in these systems allows one to use any reasonable choice of average molecular weight to determine the viscosity exponent. The study discussed below gives a better test of which choices of average molecular weight are consistent with a power law viscosity–molecular weight relation.

4. Polystyrene Blends

Friedman and Porter[18] have emphasized that well-separated bimodal distributions yield a strong separation between different average molecular weights, varying considerably over the mixing range, and consequently provide a much more sensitive indication of the form of the viscosity–molecular weight relation than systems with unimodal distributions. In this way they have explicitly demonstrated that M_w continues to yield a linear log η–log $\bar{M}$ relation but that M_n, M_z, and various other AMWs fail to give a constant viscosity exponent. By assuming a form for the molecular weight distribution, we can add M^* to their list of unsuitable AMWs. The approach given here differs from that of the previous two sections in that we actually compute the various average molecular weights and plot them against quoted values of the viscosity.

To compute M^* for blends of known components we extend the formulas of Friedman and Porter and derive in Appendix B the general mixing law

$$[\alpha]_i = \frac{[\alpha - 1]_i}{[\alpha - 1]_i + \sum_{\substack{j=1 \\ j \neq i}}^{2} ({}^jM_{\alpha-1}/{}^iM_{\alpha-1})[\alpha - 1]_j} \qquad (4.1)$$

and the general blending law

$${}^{B}M_\alpha = [\alpha]_1 \cdot {}^1M_\alpha + [\alpha]_2 \cdot {}^2M_\alpha \qquad (4.2)$$

for the α-order average molecular weight of the blend. Equation 4.1 gives the α-order fraction of component i in terms of the lower order AMWs ${}^{1,2}M_{\alpha-1}$ and the lower order fractions $[\alpha - 1]_{1,2}$ of both components. In this notation $[1]_i$ denotes the weight fraction w_i and ${}^iM_1$ the weight-average molecular weight ${}^iM_w$ of the ith component.

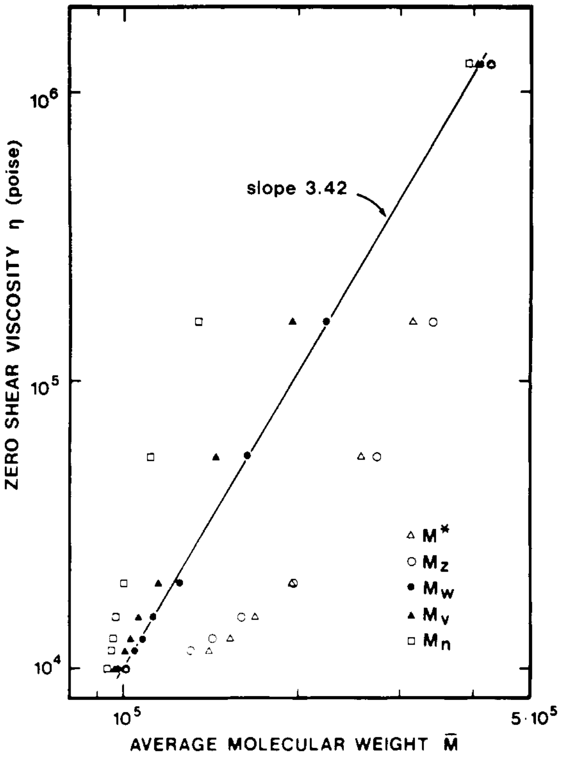

Figure 3. Viscosity–molecular weight dependence for various average molecular weights for the two-component blend data of Prest and Porter.[19] M^* is defined in eq 1.5. M_v is computed with $q = 0.5$ (see Appendix C). Data for eight mixtures is shown, with each end point corresponding to one of the two narrow-distribution components. Solid line: least-squares fit $\eta \propto M_w^{3.42}$.

Higher order component fractions follow from the known weight fractions w_1 and w_2 by recursive use of eq 4.1, and when employed in eq 4.2, they enable us to determine the required higher order moments of the blend molecular weight distribution from the higher order moments for the individual components. The latter are determined from available data and, when necessary, from a model molecular weight distribution. The value of M^* in the blend is then given by ${}^{B}M^* = [{}^{B}M_1 \cdot {}^{B}M_2 \cdot {}^{B}M_3]^{1/3}$, following eq 1.5. Additionally, the formula

$$ {}^{B}M_v = (w_1 \cdot {}^{1}M_v^{q} + w_2 \cdot {}^{2}M_v^{q})^{1/q} \qquad (4.3)$$

determines the viscosity-average molecular weight of the blend and follows by combining eq C.2 and B.10.

Applying these expressions to the well-documented blend data of Prest and Porter,[19] we plot log η against log $\bar{M}$ in Figure 3 for the average molecular weights $\bar{M} = M^*$, M_{z+1}, M_w, M_v, and M_n. Such a plot is preferable to Friedman and Porter's w_2–log η graph because our plot does not a priori assume a value for the viscosity exponent. To compute $M_3 = M_{z+1}$ and M_v we assumed a log-normal molecular weight distribution for the individual unimodal components. Considering the acceptability of the fit to the empirical molecular weight distributions of Onogi et al. shown in Figure 1 and the fact that the components blended by Prest and Porter were also produced by anionic polymerization, this is a reasonable assumption.

We see from the blend data of Prest and Porter that only M_w can have a linear log η–log $\bar{M}$ relation and that the prediction from reptation theory[6,7] of a constant viscosity exponent for M^* is quite strongly ruled out.

5. Conclusion

In this paper we have computed the possible effects of polydispersity on the molecular weight dependence of the zero-shear melt viscosity by modeling the molecular weight distributions of polymer melts.

General considerations indicate that if the *rate* of variation in polydispersity from sample to sample is sufficiently high, then substantial changes in the viscosity–molecular weight relation must occur when reexpressed in terms of different average molecular weights. In such cases only one kind of zero-shear viscosity exponent can be constant with increasing molecular weight; existing data show that log η is linear against log M_w, but certainly not against log M_v, log M_n, log M_z, or log M^*, among other average molecular weights.

For melt samples obtained by anionic polymerization, with a very small *rate* of polydispersity variation, the viscosity exponent is insensitive to reasonable changes in the type of average molecular weight used. This rules out any significant corrections in the viscosity exponent as a result of choosing an "incorrect" average molecular weight. Since measured values of this exponent typically exceed 3, with the often-quoted value being 3.4, it is clear that there is a real discrepancy between observations and the prediction of reptation theory. Although it may have other causes, this discrepancy cannot be explained away by polydispersity effects through modification of the choice of average molecular weight.

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Appendix A

We give an analysis of the way in which least-squares-fit parameters describing a set of data are modified when the data values are perturbed. We do this for a simple case relevant to the discussion of section 3. The original and altered sets of observations are denoted by $\{X_i,Y_i\}_{i=1...N}$ and $\{X_i',Y_i\}_{i=1...N}$, respectively. Thus the perturbation in the data is assumed to take place in the X components alone. We deal with a linear fit $Y = aX + b$, whose parameters are a and b.

Our particular interest is in comparing the values of the fitted slopes $\langle a \rangle$ and $\langle a' \rangle$ for the initial and final sets of data. For this purpose it is convenient to define a particular function $(\mathbf{X},\mathbf{Y})$ of the N-component observation vectors $\mathbf{X}$ and $\mathbf{Y}$. It is

$$(\mathbf{X},\mathbf{Y}) = \sum_{i=1}^{N} X_i Y_i - \sum_{i=1}^{N} X_i \sum_{i=1}^{N} Y_i / N \qquad (A.1)$$

This is a symmetric bilinear form and has the additional property

$$(\mathbf{X},\mathbf{1}) = 0 \qquad (A.2)$$

where $\mathbf{1}$ denotes the vector (1, 1, ..., 1). The general expression for the slope in a linear least-squares fit is then given by

$$\langle a \rangle = (\mathbf{X},\mathbf{Y})/(\mathbf{X},\mathbf{X}) \qquad (A.3)$$

With the perturbed set of data the slope becomes

$$\langle a' \rangle = (\mathbf{X}',\mathbf{Y})/(\mathbf{X}',\mathbf{X}') \qquad (A.4)$$

We describe the deviations of the original data from the fit by the vector Δ, defined by

$$\Delta = Y - [\langle a \rangle \mathbf{X} + \langle b \rangle \mathbf{1}] \qquad (A.5)$$

where $\langle b \rangle$ denotes the fitted y intercept. Substituting for $\mathbf{Y}$ in eq A.4 and using eq A.2, we obtain

$$\langle a' \rangle = \langle a \rangle \frac{(\mathbf{X}',\mathbf{X})}{(\mathbf{X}',\mathbf{X}')} + \frac{(\mathbf{X}',\Delta)}{(\mathbf{X}',\mathbf{X}')} \qquad (A.6)$$

Noting that $(\boldsymbol{\Delta},\mathbf{X}) = 0$, and $\langle a'\rangle\cdot(\mathbf{X}',\mathbf{X}') = (\mathbf{X}',\mathbf{Y})$, we can divide by $\langle a'\rangle$ and rewrite this as

$$\frac{\langle a'\rangle}{\langle a\rangle} = \frac{(\mathbf{X}',\mathbf{X})}{(\mathbf{X}',\mathbf{X}')}\left\{1 - \frac{(\delta\mathbf{X},\boldsymbol{\Delta})}{(\mathbf{X}',\mathbf{Y})}\right\}^{-1} \tag{A.7}$$

where $\delta\mathbf{X} \equiv \mathbf{X}' - \mathbf{X}$. Consequently, when both the deviations from a linear fit and the perturbations in the X observations are small, we obtain

$$\frac{\langle a'\rangle}{\langle a\rangle} \simeq \frac{(\mathbf{X}',\mathbf{X})}{(\mathbf{X}',\mathbf{X}')} \tag{A.8}$$

This result is employed in section 3.

This expression is very useful since it only involves the values of the X observations. Unfortunately, it is impossible to exactly determine the size of the correction term contained in eq A.7 when the Y observations are unavailable. However, it is possible to estimate its magnitude from the X observations. First, by interchanging the initial and final observations in eq A.7 we immediately have

$$\frac{\langle a\rangle}{\langle a'\rangle} = \frac{(\mathbf{X},\mathbf{X}')}{(\mathbf{X},\mathbf{X})}\left\{1 + \frac{(\delta\mathbf{X},\boldsymbol{\Delta}')}{(\mathbf{X},\mathbf{Y})}\right\}^{-1} \tag{A.9}$$

where

$$\boldsymbol{\Delta}' = \mathbf{Y} - [\langle a'\rangle\mathbf{X}' + \langle b'\rangle\mathbf{1}] \tag{A.10}$$

Multiplying eq A.9 by eq A.7 we then find

$$\frac{(\mathbf{X},\mathbf{X}')}{(\mathbf{X},\mathbf{X})}\,\frac{(\mathbf{X}',\mathbf{X})}{(\mathbf{X}',\mathbf{X}')} = 1 + \frac{(\delta\mathbf{X},\boldsymbol{\Delta}')}{(\mathbf{X},\mathbf{Y})} - \frac{(\delta\mathbf{X},\boldsymbol{\Delta})}{(\mathbf{X}',\mathbf{Y})} - \frac{(\delta\mathbf{X},\boldsymbol{\Delta}')}{(\mathbf{X},\mathbf{Y})}\,\frac{(\delta\mathbf{X},\boldsymbol{\Delta})}{(\mathbf{X}',\mathbf{Y})} \tag{A.11}$$

Thus we estimate the correction term to be

$$\left|\frac{(\delta\mathbf{X},\boldsymbol{\Delta})}{(\mathbf{X}',\mathbf{Y})}\right| \simeq \left|\frac{(\delta\mathbf{X},\boldsymbol{\Delta}')}{(\mathbf{X},\mathbf{Y})}\right| \simeq \left|1 - \frac{(\mathbf{X},\mathbf{X}')^2}{(\mathbf{X},\mathbf{X})(\mathbf{X}',\mathbf{X}')}\right| \tag{A.12}$$

In the case of the data analyzed in section 3 and summarized in Table II, we find the correction to the ratio $\langle a_{M^*}\rangle/\langle a_{M_w}\rangle = 1.023$ to be 0.0012 with the log-normal model molecular weight distribution. For the ratio $\langle a_{M_v}\rangle/\langle a_{M_w}\rangle = 0.994$ it is 0.00007. These adjustments are insignificant.

Appendix B

We derive expressions that give the moments of the molecular weight distribution of a blend in terms of the moments and weight fractions of the components which are mixed to form the blend. Extensive quantities are signified by upper case letters or round brackets, and intensive quantities by lower case letters or square brackets.

We begin by recalling the various ways of describing a general distribution of molecular weights.[20] Our starting point is the number distribution N_M, which gives the number of molecules at each molecular weight M. In itself, the number distribution completely characterizes the sample, but a more general description is useful. This is obtained by weighting each molecular weight by M^α and is called the extensive α-order distribution

$$(\alpha)_M = M^\alpha N_M \tag{B.1}$$

From this we can define the α-order total over all molecular weights

$$(\alpha) = \sum_M (\alpha)_M \tag{B.2}$$

For example, the total number of molecules, N, is obtained with $\alpha = 0$ and is written $N = (0)$, while the total weight, W, is $W = (1)$. For a normalized description we define the intensive α-order distribution

$$[\alpha]_M = (\alpha)_M/(\alpha) \tag{B.3}$$

Using this, we can specify $\langle M^\gamma\rangle_\alpha$, the γ-order moment with respect to the α-order distribution. It is

$$\langle M^\gamma\rangle_\alpha = \sum_M [\alpha]_M \cdot M^\gamma \tag{B.4}$$

With $\gamma = 1$ and $\alpha = 0$, 1, 2, and 3, this reduces to the familiar average molecular weights M_n, M_w, M_z, and M_{z+1}. In section 4 we denoted these collectively by M_α.

Since distributions referring to quantity are additive, the extensive α-order distribution ${}^{B}(\alpha)_M$ of a blend is the sum of the corresponding distributions $\{{}^{i}(\alpha)_M\}_{i=1\ldots N_c}$ of each of its N_c components. That is

$${}^{B}(\alpha)_M = \sum_i {}^{i}(\alpha)_M \tag{B.5}$$

The same applies to the α-order total ${}^{B}(\alpha)$ of the blend:

$${}^{B}(\alpha) = \sum_i {}^{i}(\alpha) \tag{B.6}$$

It then follows from the general definition eq B.3 that the intensive α-order distribution of the blend is

$${}^{B}[\alpha]_M = \sum_i [\alpha]_i \cdot {}^{i}[\alpha]_M \tag{B.7}$$

In this equation ${}^{i}[\alpha]_M$ is the intensive α-order distribution of the ith component

$${}^{i}[\alpha]_M = {}^{i}(\alpha)_M/{}^{i}(\alpha) \tag{B.8}$$

and $[\alpha]_i$ is the α-order fraction in the blend of component i

$$[\alpha]_i = {}^{i}(\alpha)/{}^{B}(\alpha) \tag{B.9}$$

In more familiar terms, $[0]_i$ is the number fraction n_i while $[1]_i$ is the weight fraction w_i. Upon multiplying eq B.7 by M^γ and summing over M, we see that the general moment ${}^{B}\langle M^\gamma\rangle_\alpha$ of the blend is given in terms of the corresponding moments $\{{}^{i}\langle M^\gamma\rangle_\alpha\}_{i=1\ldots N_c}$ of each component by the blending law

$${}^{B}\langle M^\gamma\rangle_\alpha = \sum_i [\alpha]_i \cdot {}^{i}\langle M^\gamma\rangle_\alpha \tag{B.10}$$

To use eq B.10 it is also necessary to know the α-order component fractions $\{[\alpha]_i\}_{i=1\ldots N_c}$ defined in eq B.9. This can be determined from the component weight fractions $\{w_i\}_{i=1\ldots N_c}$ provided the moments ${}^{i}M_\beta$ are known for each component for $\beta = 1, \ldots, \alpha - 1$. To see this we observe from eq B.1 that in general

$$(\alpha)_M = M^\beta \cdot (\alpha - \beta)_M \tag{B.11}$$

so that with eq B.2 to B.4 we have

$$(\alpha) = \langle M^\beta\rangle_{\alpha-\beta} \cdot (\alpha - \beta) \tag{B.12}$$

The special case $\beta = 1$ gives

$$(\alpha) = M_{\alpha-1} \cdot (\alpha - 1) \tag{B.13}$$

where we write $M_{\alpha-1}$ for $\langle M_{\alpha-1}\rangle$. This result applies to each component i, and when used in eq B.9, it yields

$$[\alpha]_i = {}^{i}M_{\alpha-1} \cdot {}^{i}(\alpha - 1)\Big/\sum_j {}^{j}M_{\alpha-1} \cdot {}^{j}(\alpha - 1) \tag{B.14}$$

Dividing numerator and denominator by ${}^{i}M_{\alpha-1} \cdot {}^{B}(\alpha - 1)$ and rearranging, we find

$$[\alpha]_i = \frac{[\alpha - 1]_i}{[\alpha - 1]_i + \sum\limits_{\substack{j=1 \\ j\neq i}}^{N_c} ({}^{j}M_{\alpha-1}/{}^{i}M_{\alpha-1})[\alpha - 1]_j} \tag{B.15}$$

When this equation is used recursively, it determines $[\alpha]_i$ in terms of $\{w_j, {}^jM_1, {}^jM_2, ..., {}^jM_{\alpha-1}\}_{j=1...N_c}$.

For completeness we also note that

$$[\alpha]_i = \frac{[\alpha + 1]_i}{[\alpha + 1]_i + \sum_{\substack{j=1 \\ j\neq i}}^{N_c} ({}^iM_\alpha/{}^jM_\alpha)[\alpha + 1]_j} \qquad (B.16)$$

This result can be obtained by similar reasoning using

$$(\alpha) = (\alpha + 1)/M_\alpha \qquad (B.17)$$

Equation B.17 follows from eq B.12 and the general result

$$\langle M^{\gamma+\mu}\rangle_\alpha = \langle M^\gamma\rangle_\alpha \cdot \langle M^\mu\rangle_{\alpha+\gamma} \qquad (B.18)$$

with $\gamma = 1$ and $\mu = -1$. Equation B.18 can be derived from eq B.11 and B.4.

These results generalize those given by Friedman and Porter.[18]

Appendix C

We demonstrate that the viscosity-average molecular weight M_v is less than the weight-average molecular weight M_w for any molecular weight distribution w_M.

The argument is based on the Holder inequality[21]

$$\sum_i |a_i b_i| \leq (\sum_i |a_i|^\lambda)^{1/\lambda} (\sum_i |b_i|^\mu)^{1/\mu} \qquad (C.1)$$

where $\lambda, \mu > 1$ such that $\lambda^{-1} + \mu^{-1} = 1$, and on the definition of M_v, namely

$$M_v{}^q = \sum_M w_M M^q \qquad (C.2)$$

where w_M denotes the weight fraction at M and q depends on the polymer–solvent interaction. Equation C.2 also defines M_w if q is replaced by unity. So when $q > 1$, we let $\lambda = q$, $a_M = w_M{}^{1/\lambda}M$, and $b_M = w_M{}^{1/\mu}$ and substitute in eq C.1 to obtain $M_v \geq M_w$. If $q < 1$, we put $\lambda = 1/q$, $a_M = w_M{}^{1/\lambda}M^{1/\lambda}$, and $b_M = w_M{}^{1/\mu}$ to obtain $M_v \leq M_w$. Usually[22] one has $0.5 < q < 0.8$ and thus $M_v \leq M_w$.

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Predicting the Shift in Viscoelastic Response Caused by Physical Aging of Glassy Polymers†

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ABSTRACT: Measurements of the specific volume of a poly(vinyl acetate) glass during isothermal annealing at 25 and 30 °C are analyzed theoretically to predict the shift in the time scale of viscoelastic response. These predictions agree with direct measurements of the change in the viscoelastic shift factor of the poly(vinyl acetate) at those temperatures. Both the volume and shift factor measurements were taken from literature reports of Kovacs, Stratton, and Ferry. Our predictive method is based on an extension into the glassy state of Simha and Somcynsky's theory for the equation of state of polymeric liquids. Analysis of the volume changes with that theory yields a time-dependent fraction of free volume. This free volume fraction is then substituted into the Doolittle equation to predict the shift in viscoelastic response. Our method had been tested previously with measurements on an isothermally annealed poly(methyl methacrylate) glass, but we consider the present test with the poly(vinyl acetate) results to be more rigorous.

Introduction

It is well-known that polymer glasses prepared by cooling from the liquid state exhibit spontaneous changes in certain physical properties.[1] For example, isothermal annealing causes a change in their specific volume and a shift in the time scale of their viscoelastic response. Predicting the time shift in viscoelastic response from measurements of the volume change is the subject of this work.

Recently, the present authors and R. Simha proposed[2] that a theoretical equation of state for amorphous polymers[3] could be utilized to make the prediction. In particular, we analyzed volume changes with that theory to yield a time-dependent fraction of unoccupied volume. This free volume fraction was then substituted into the Doolittle equation to predict the shift in viscoelastic response. The results of our analysis agreed with some viscoelastic measurements[4] taken during annealing of a

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