

A Relationship Between Steady-State Shear Melt Viscosity and Molecular Weight Distribution in Polystyrene

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Synopsis

A model that relates to the molecular weight distribution (MWD) of high-density polyethylene to the steady-state shear melt viscosity has been applied to polystyrene melts. Relations are developed for predicting the rheological flow curve from the molecular weight distribution. Relationships are also developed to predict the MWD from the flow curve, although practical limitations to this procedure are given. From a consideration of predictions of the model and experimental data, it is concluded that the transition for a given molecular species from Newtonian to non-Newtonian flow is sharp. Additionally, the calculated empirical parameter that partitions the MWD into molecules that act in a Newtonian fashion and those that do not is shown to be equivalent to the largest molecular weight homolog that can still undergo Newtonian flow at a given shear rate for monodisperse fractions. The temperature dependence of the relaxation times is found to be somewhat higher than that predicted by the Rouse theory. An activation energy of 30 kcal/mole for η_0 was used to fit the experimental viscosity data adequately at 190° and 225°C. The terminal relaxation spectrum for a narrow-MWD polystyrene standard is calculated and found to agree well for long relaxation times with that reported in the literature.

INTRODUCTION

A model relating the non-Newtonian steady-shear melt viscosity, relaxation spectrum, and elastic properties of high-density polyethylene to the molecular weight distribution, MWD, has been described in earlier publications.^{1,2} *The model is based upon the concept that viscoelastic functions at zero shear rate are valid at nonzero shear rates if the shear-dependent contributions of the molecular components are individually taken into account.* The model can best be described in terms of four major assumptions about the effect of shear rate on the spectrum of relaxation times. First, it is assumed that the spectrum of relaxation times is cut off at a maximum allowed relaxation time, $\tau_m(\dot{\gamma})$. Second, it is assumed that the τ_m is a function of shear rate such that $\tau_m \propto 1/\dot{\gamma}$. The third assumption is that, in addition to the longest relaxation time for a given molecule, the molecular chain undergoes relaxations characteristic of all molecular weight molecules less than its own molecular weight. Lastly, it is assumed that the relaxation times associated with a given molecular species are independent of communal properties in a polydisperse sample. This last assumption is restricted to entangled systems.

The first assumption given above suggests that the general relation³ for the zero shear viscosity to the relaxation spectrum may be modified to

$$\eta(\dot{\gamma}) = \int_0^{\tau_m} H(\tau) d\tau \quad (1)$$

The effect of shear rate on the relaxation spectra for two monodisperse species of differing molecular weight is schematically shown in Figure 1. The third assumption implies that, for relaxation times less than or equal to the longest relaxation time of the smaller molecular weight species M_1 in Figure 1, the relaxation spectra of the two samples of differing molecular weight are identical. Furthermore, the behavior depicted in the figure indicates that the effective (operative) relaxation spectra will be the same at any shear rate where both samples are undergoing non-Newtonian flow. However, from eq. (1), this implies that both samples will have identical viscosities (equivalent to that of a sample of molecular weight M_c , which has as its longest relaxation time τ_m). In other words, at a given shear rate, all molecular weight species larger than M_c act as though they were of molecular weight M_c , and species having molecular weights less than M_c act as they do at zero shear. M_c can be thought of as the largest molecular weight homolog that can be undergoing Newtonian flow at a given shear rate.

The above argument also suggests that the onset of non-Newtonian flow is due to the rendering inoperative of the longest relaxation time associated with the sample. Similar ideas have been expressed by Vinogradov³ in explaining the effects of blending of narrow-MWD polybutadienes on the land fracture phenomenon. Vinogradov suggests that each component of the mixture acts independently and that each component either contributes to the viscous losses as it does in the Newtonian region or acts with diminished effect in the high elastic state.

In order to calculate the steady-state shear viscosity at any shear rate for broad-MWD polymers, the relation between zero shear viscosity and molecular weight was assumed to be known. An empirical relationship for polyethylene at 190°C reported in the literature⁴ was used:

$$\log \eta_0 = -12.296 + 3.36 \log \bar{M}_w + 0.51 \log (\bar{M}_z / \bar{M}_w) \quad (2)$$

The steady shear melt viscosity at any shear rate was assumed to be related to the MWD through the relation

$$\log \eta(\dot{\gamma}) = -12.296 + 3.36 \log \bar{M}_w^* + 0.51 \log [\bar{M}_z^* / \bar{M}_w^*]$$

where

$$\begin{aligned} \bar{M}_w^* &= \sum_{i=1}^{i=c-1} w_i M_i + M_c \sum_{i=c}^{\infty} w_i \\ \bar{M}_z^* &= \sum_{i=1}^{i=c-1} w_i M_i^2 + M_c^2 \sum_{i=c}^{\infty} w_i / \left[\sum_{i=1}^{i=c-1} w_i M_i + M_c \sum_{i=c}^{\infty} w_i \right] \end{aligned} \quad (3)$$

and w_i is the weight fraction of the i th component. For high-density polyethylene, the relation between M_c and $\dot{\gamma}$ was found to be

$$M_c = 540,000 (\dot{\gamma}^{-0.300}) \quad (4)$$

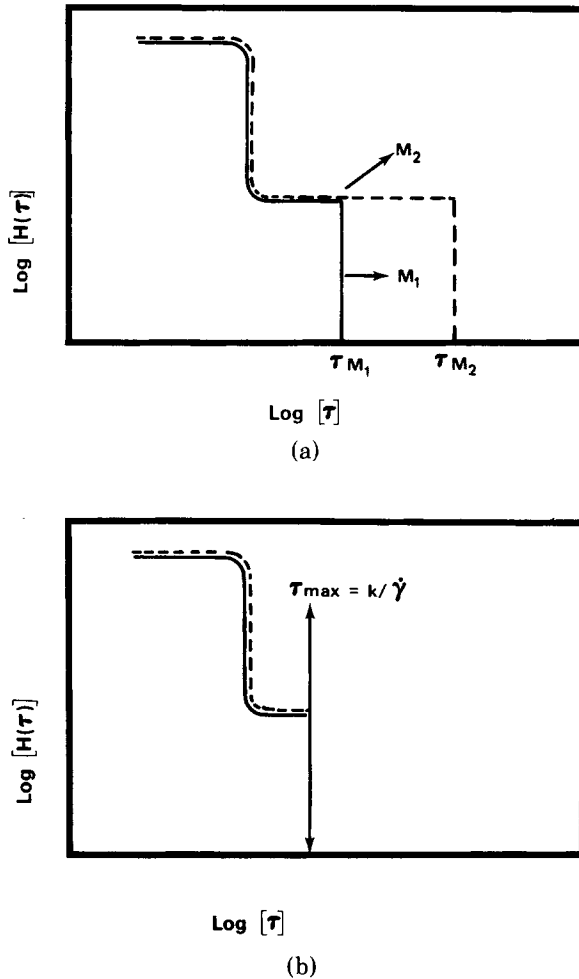


Fig. 1. (a) Schematic view of the relaxation spectra at zero shear rate of two monodisperse samples having molecular weights M_1 and M_2 , where $M_2 > M_1$. (b) Postulated effect of shear rate on the relaxation spectra of the two samples in (a). In the case depicted, both samples would be undergoing non-Newtonian flow.

In spite of the model's success in accounting for the variation of viscosity and first normal stress difference as a function of shear rate, a number of important questions remain unanswered. The most pressing question involves the definition of M_c . In our model, the empirically determined relation of M_c to shear rate for polydisperse samples is assumed to be the variation of the onset of non-Newtonian flow for monodisperse samples of varying molecular weight with shear rate. Unfortunately, no essentially monodisperse samples of HDPE are readily available to test the above assumption. At this point, M_c (as calculated from a broad-MWD sample) must be regarded as an empirical parameter whose exact meaning remains to be defined. This is one of the goals of this publication. We shall attempt to give meaning to M_c by generating a M_c -versus-shear rate relationship similar to eq. (4) for a broad MWD and comparing this relationship with the onset of non-Newtonian behavior in very narrow-MWD samples.

Polystyrene is an ideal polymer with which to test the definition of M_c since

quite narrow-MWD anionically polymerized polystyrene materials are readily available. Using these materials, the model's assumption of a sharp transition from Newtonian to non-Newtonian flow can also be tested. Further, the generality of the "partition" model can be assessed, and inversion of the model to predict the MWD from rheological data will be demonstrated. In a manner similar to that used for HDPE,² the terminal relaxation spectrum for a narrow-MWD polystyrene standard will also be shown to be predictable from the parameteric relations as obtained from a broad-MWD sample.

EXPERIMENTAL

The sample labeled PS-350 is a commercial crystal polystyrene. The polystyrene standards were anionically polymerized materials obtained from ArRo Laboratories.

Rheological data were obtained at 190° and 225°C using an Instron rheometer with a capillary having an L/D of 33:1. Rabinowitsch corrections were applied to the data.

Molecular weight data were obtained on a Waters Model 200 GPC at 135°C using 1,2,4-trichlorobenzene as a solvent and four Styrogel columns of porosities 10^6 , 10^5 , 10^4 , and 10^3 Å. Polystyrene standards polymerized by Pressure Chemical and characterized by ArRo Laboratories were used for calibration. Spreading corrections⁵ were applied to the molecular weight distribution data for the anionically polymerized standards used in this study to obtain the polydispersities as given by ArRo Laboratories.

RESULTS AND DISCUSSION

Calculation of the Relation Between M_c and Shear Rate for Polystyrene

In order to calculate the relation between M_c and shear rate, the relationship between zero shear viscosity and molecular weight must be known. The relationship given by Zosel⁶ was chosen as

$$\log \eta_0 = -12.8 + 3.4 \log \bar{M}_w \quad \text{at } 190^\circ\text{C} \quad (5)$$

To find the relation at 225°C, an activation energy of 30 kcal/mole as given by various authors⁷⁻⁹ was used to give

$$\log \eta_0 = -13.8 + 3.4 \log \bar{M}_w \quad \text{at } 225^\circ\text{C} \quad (6)$$

Log-log plots of η versus $\dot{\gamma}$ for sample PS-350 at 190 and 225°C are given in Figure 2, where the points represent experimental data from the capillary rheometer. The MWD data for this sample are given in Table I. The value of M_c was determined at each shear rate and temperature by means of an interval halving computer program and the equation

$$\log \eta(\dot{\gamma}) = \log K + 3.4 \log \bar{M}_w^* \quad (7)$$

where $\bar{M}_w^* = \sum_{i=1}^{c-1} w_i M_i + M_c \sum_{i=c}^{\infty} w_i$, w_i is the weight fraction of the i th component from the MWD curve, and K is the constant in the zero shear viscosity relationship (i.e., $\log K = -12.8$ and -13.8 at 190° and 225°C, respectively). The

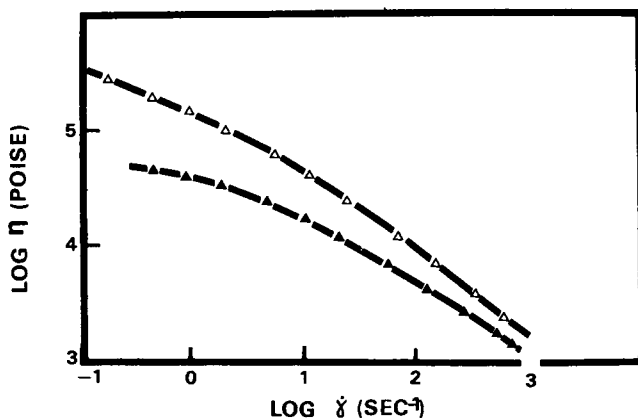


Fig. 2. Apparent viscosity η as a function of shear rate for the polystyrene sample PS-350. Solid (\blacktriangle) and open triangles (Δ) are experimental data at 225° and 190°C, respectively. The curves are the calculated relations based on eqs. (7), (8), and (9).

results of the calculations are plotted in Figure 3. The equations relating M_c and shear rate at 190° and 225°C, respectively, are given by

$$M_c = 330,000 (\dot{\gamma}^{-0.2602}) \quad (8)$$

and

$$M_c = 640,000 (\dot{\gamma}^{-0.2602}) \quad (9)$$

Comparison with High-Density Polyethylene

Figure 3 shows that, at 190°C and a given shear rate, the M_c value for polyethylene is slightly larger than that of polystyrene. Because M_c has previously been defined as the largest molecule that can still relax at a given shear rate, it may be concluded that, at 190°C and at a given shear rate, a larger molecular weight molecule of polyethylene may more fully relax than that of polystyrene. However, because the activation energies for polyethylene and polystyrene are so different (i.e., approximately 6.3 kcal for polyethylene vs approximately 30 kcal for polystyrene), the relative M_c values change substantially with temperature.

The relations of $\log M_c$ vs $\log \dot{\gamma}$ for polystyrene at 190° and 225°C have the

TABLE I
Molecular Weight Distribution Data for the Polystyrene Samples

Sample	\bar{M}_n	\bar{M}_w	\bar{M}_z	\bar{M}_w/\bar{M}_n
PS-350	72,000	290,000	580,000	5.4
PS-1	158,000 ^a	179,000 ^a		1.13
PS-2	375,000 ^a	411,000 ^a		1.10
PS-3	735,000 ^a	852,000 ^a		1.16

^a Average values given by ArRo Laboratories.

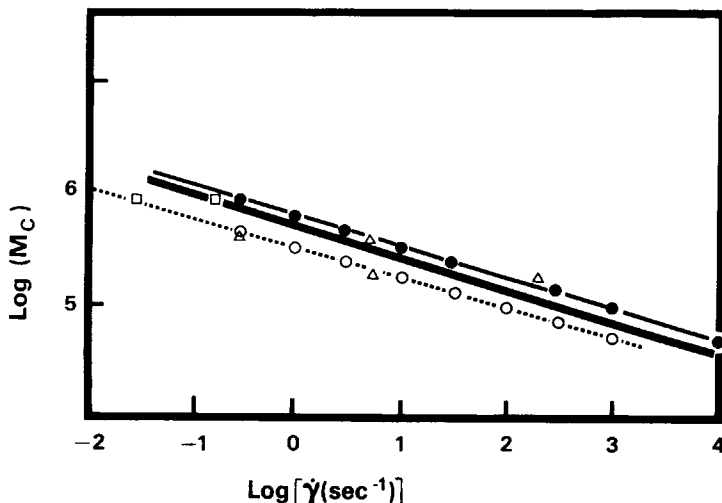


Fig. 3. Relation between partitioning molecular weight M_c and shear rate. Solid black and open circles are calculated points from polystyrene sample PS-350 at 225° and 190°C, respectively. Triangles are points based on the narrow-MWD Pressure Chemical polystyrene standards of $\bar{M}_w = 411,000$ and $\bar{M}_w = 160,000$. These points were obtained from the data of Graessley and Penwell.¹¹ Squares were calculated from the data of Chee and Rudin. Heavy solid line is that obtained earlier for high-density polyethylene.²

same slope. Calculating¹ the limiting power law relation between viscosity and shear rate for polystyrene as $3.4 \times$ slope, we obtain a value of -0.88 , which is higher than the -0.818 as predicted by Graessley¹⁰ and somewhat lower than the value of -1.0 predicted from the model presented for polyethylene¹ of -1.0 .

Prediction of the Flow Curve for "Essentially Monodisperse Samples"

The model assumes that M_c is a unique (for a given polymer structure) function of shear rate and that there is a sharp transition from Newtonian to non-Newtonian flow for either a monodisperse sample or a homolog in a polydisperse sample. These assumptions can be tested by applying the M_c -versus-shear-rate relationship as obtained on a broad-MWD polystyrene sample to essentially monodisperse, anionically polymerized polystyrene standards of known molecular weight.

Experimental data for a Pressure Chemical standard of $\bar{M}_w = 411,000$ from Graessley's¹¹ cone-and-plate rheometer and our Instron rheometer at 190°C are given in Figure 4. The data of Graessley are those obtained at 193.5°C. The data have been shifted both vertically and horizontally to correspond to 190°C data assuming an E_a of 30 kcal/mole for η_0 . The solid curve is that predicted on the basis of molecular weight distribution data corrected for spreading⁵ so as to yield $\bar{M}_w/\bar{M}_n = 1.1$ and $\bar{M}_w = 411,000$. The agreement is quite good. Because the predictions are based on a sharp transition from Newtonian to non-Newtonian behavior for each homolog in the very narrow-MWD sample, the assumption of a sharp transition is reinforced. Furthermore, the generality of the M_c -versus-shear-rate relation is demonstrated. Additionally, the

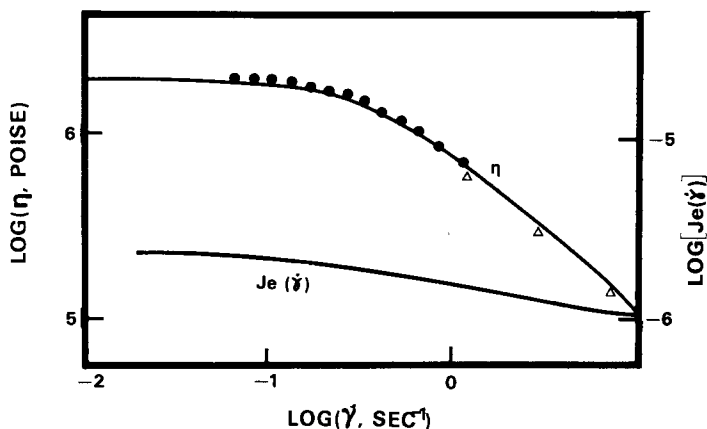


Fig. 4. Apparent viscosity η and steady shear elastic compliance J_e at 190°C for the Pressure Chemical standard having $\bar{M}_w = 411,000$ and $\bar{M}_w/\bar{M}_n = 1.1$. Solid circles are experimental viscosity data from Graessley¹¹ obtained on the cone-and-plate viscometer. Triangles are experimental data obtained on the capillary rheometer.

agreement obtained here on the Pressure Chemical sample having $\bar{M}_w = 411,000$ should be general for the other narrow-MWD standards, since at equivalent polydispersities the shapes of the viscosity–shear-rate curves can be quantitatively superimposed.¹¹

Comparison of Partitioning Molecular Weight M_c (as Calculated from a Polydisperse Sample) with Onset of non-Newtonian Flow Observed for Essentially Monodisperse Samples

Ideally, it would be desirable to obtain the shear rate at which flow changes from Newtonian to non-Newtonian for a group of monodisperse polystyrene samples of different molecular weights in order to verify that M_c (as calculated from a broad-MWD sample) is the same as the onset of non-Newtonian flow for a monodisperse sample of molecular weight M_c . However, narrow-MWD polystyrene samples of $\bar{M}_w/\bar{M}_n \approx 1.1$ do not suit this type of analysis since even this small amount of polydispersity leads to a fairly broad transition from Newtonian flow to power law behavior. In principle, the shear rate at which non-Newtonian behavior just begins could be used to calculate the corresponding M_c , and the result could be compared with the largest molecular weight observed by GPC. However, neither the shear rate for the onset of non-Newtonian flow nor the largest molecular weight homolog in the sample can be accurately determined.

As a result of the difficulties, a better approach is to use \bar{M}_w , which is presumably more accurately known. A log normal MWD will be assumed. It is shown in the Appendix that the melt viscosity for samples of $\bar{M}_w/\bar{M}_n = 1.10$ and 1.16 and having log normal MWD's will drop to 65% and 57%, respectively, of the viscosity at zero shear when the shear rate is reached such that $M_c = \bar{M}_w$. Consequently, since \bar{M}_w is known and the $\dot{\gamma}$ at which $\eta/\eta_0 = 0.65$ (or 0.57 for $\bar{M}_w/\bar{M}_n = 1.16$) can be measured, a point is independently determined that can be compared to the relationship obtained for the broad-MWD sample in Figure 3.

Using the criterion that $M_c = \bar{M}_w$ when $\eta/\eta_0 = 0.65$ (or 0.57 for $\bar{M}_w/\bar{M}_n = 1.16$), the shear rate at which $\eta/\eta_0 = 0.65$ vs \bar{M}_w is plotted in Figure 3 for three polystyrene standards at 190° and 225°C. The 190°C data on PS-1 and PS-2 were interpolated from the data of Graessley.¹¹ The 225°C data were obtained from an extrapolation of Graessley's¹¹ data and are not as accurate as those at 190°C. The data at 190° and 225°C for PS-3 were calculated from the data of Chee and Rudin.¹² As can be seen in Figure 3, these points as determined for the three narrow-MWD standards agree well with the log M_c -vs-log $\dot{\gamma}$ relations established from the broad-MWD sample PS-350. It, therefore, may be concluded that M_c is well defined as the largest molecular weight species that acts in a Newtonian fashion at a given shear rate.

Relaxation Times

As shown in an earlier publication² on the prediction of elastic properties from MWD, the steady shear elastic compliance can be calculated in terms of the unknown parameter β , which represents the proportionality constant in the assumed relation between the maximum allowed relaxation time τ_m and $1/\dot{\gamma}$. (The onset of non-Newtonian flow is interpreted as the disappearance of a relaxation time proportional to $1/\dot{\gamma}$.) Using the experimental results of Mieras and Rijn,¹³ we found β to be 1.65. Consequently, for polystyrene,

$$\tau_m = 1.65/\dot{\gamma} \quad (10)$$

and from eq. (8),

$$\tau = 1.0 \times 10^{-21} M^{3.84} \quad (11)$$

The constant of 1.65 for polystyrene at 190°C in eq. (10) is almost identical to that of 1.7 obtained for polyethylene at 190°C. While the agreement between these two constants suggests a unique value for β , which is independent of polymer type, the sensitivity of this constant to the choice of zero shear relations for the two different polymer systems and the sensitivity of this constant to the various calculations made in obtaining it make the agreement seem fortuitous.

The temperature dependence of the relaxation times can be calculated from eqs. (8) and (9). From the assumed proportionality between the maximum allowed relaxation time and $1/\dot{\gamma}$ for a given molecular weight M_c , the effect of temperature can be represented as

$$\frac{\tau_{190^\circ\text{C}}}{\tau_{225^\circ\text{C}}} = \left(\frac{640,000}{330,000} \right)^{1/0.2602} = 12.75$$

Temperature independence of the proportionality constant between the maximum allowed relaxation time and $1/\dot{\gamma}$ is assumed. For an $E_a = 30$ kcal/mole, the temperature variation of $\tau = \eta_0/\rho T$ from the Rouse theory is

$$\frac{\tau_{190^\circ\text{C}}}{\tau_{225^\circ\text{C}}} = \frac{(\eta_0)_{190^\circ\text{C}}}{(\eta_0)_{225^\circ\text{C}}} \times \frac{498}{463} \times \frac{\rho_{225^\circ\text{C}}}{\rho_{190^\circ\text{C}}} = 11.1$$

The temperature effect of the density ρ used here was that given by Chee and Rudin.¹⁴ Although the effect of temperature in the Rouse theory is somewhat less than predicted here, the predictions of the two models are in substantial

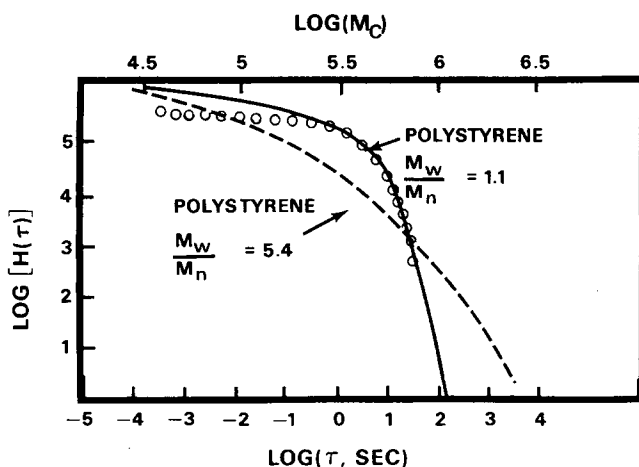


Fig. 5. Relaxation spectra for polystyrene samples PS-350 and $\bar{M}_w = 411,000$ Pressure Chemical standard as a function of relaxation time τ and partitioning molecular weight M_c . Calculated spectra for the PS-350 and Pressure Chemical standard at 190°C are given by dashed and solid line, respectively. Experimental data of Prest¹⁷ at 192°C for the Pressure Chemical material are given by circles.

agreement. The larger "shift factor" than predicted by the Rouse theory¹⁵ agrees well with the results of Graessley and Penwell¹¹ on the temperature behavior of narrow-MWD polystyrenes.

By use of the proportionality constant between relaxation time and molecular weight, α , the relaxation spectrum may be calculated (2). A similar relation to that given earlier for polyethylene is obtained as

$$H(\tau_m) = \frac{d\eta}{d\tau_m} = \frac{3.4K (\bar{M}_w^*)^{2.4} \bar{A}_2}{3.84\alpha (M_c)^{2.84}} \quad (12)$$

where

$$\bar{M}_w^* = \sum_{i=1}^{C-1} \bar{h}_i M_i + M_c \sum_{i=C}^{\infty} \bar{h}_i \quad \text{and} \quad \bar{A}_2 = \sum_{i=C}^{\infty} \bar{h}_i$$

The calculated relaxation spectra for the broad-MWD PS-350 and the 411,000 narrow-MWD samples are compared in Figure 5. Narrowing of the MWD cuts off the long relaxation times, and the terminal spectrum approaches that of a "box" as used in the theory of Maruyama et al.¹⁶ to relate the steady flow viscosity and the dynamic viscosity. The experimental data of Prest¹⁷ at 192°C are included for comparison with the calculated relaxation spectrum of the 411,000 polystyrene standard at 190°C . This agreement at the terminal end of the spectrum supports the interpretation of the shear rate for the onset of non-Newtonian behavior as the disappearance of a particular relaxation mechanism at a given shear rate. This concept is embodied in the "thixotropy theory" of Leonov and Vinogradov¹⁸ and the "network rupture theory" of Tanner.¹⁹ Furthermore, Staverman et al.²⁰ conclude that this feature is consistent with dynamic experiments superimposed on steady shearing flow.

As demonstrated for polyethylene,² the steady shear elastic compliance $J_e(\dot{\gamma})$ can be calculated once α is known. $J_e(\dot{\gamma})$ as calculated is shown in Figure 4 to be a slowly varying function of $\dot{\gamma}$. This small shear rate dependence is consistent

with those reported^{21,22} for polystyrene solutions and poly(vinyl acetate) samples. However, in contrast to the predicted decrease of $J_e(\dot{\gamma})$ with $\dot{\gamma}$, $J_e(\dot{\gamma})$ was reported by Graessley and Segal²¹ to increase slightly. Endo, Fujimoto, and Nagasawa²³ present data on poly(α -methylstyrene) consistent with the theory of Tanaka, Yamamoto, and Takino²⁴ describing the shear dependence of the shear dependent elastic compliance. Like Graessley's data, $J_e(\dot{\gamma})$ was found by Nagasawa et al. to increase with shear rate for very narrow-MWD samples.

Speculation Regarding Entanglements

In view of the "partition" model's success in describing the elastic properties and non-Newtonian viscosity behavior of both polyethylene and polystyrene melts, some discussion of the model's implications in terms of entanglements seem in order.

Although entanglements are generally accepted as the cause of the strong dependence of the zero shear viscosity on molecular weight, the origin of the non-Newtonian behavior is not so clear. If entanglements are accepted as the dominant contribution (i.e., intermolecular interactions predominate over intramolecular interactions), then the non-Newtonian behavior of high molecular weight polymers can be qualitatively accounted for in three general ways: (1) the number of entanglements vary with shear rate when a critical shear rate is exceeded; (2) the number remains the same but their effectiveness changes with shear rate; or (3) some combination of the number and effectiveness of the entanglements changes with shear rate.

If the first possibility is accepted, non-Newtonian flow implies a reduced number of couples for molecules at increased shear rates. However, in terms of the basic assumption of the partition model, the validity of application of characteristics of monodisperse to polydisperse samples, molecules in a polydisperse sample that are not undergoing non-Newtonian flow participate in the same number of couples that they do at zero shear. Therefore, we have a paradoxical situation where the number of entanglements in a presumably homogeneous sample are changed for some molecules and not for others, but they would have to participate in mutual couples for the sample to be homogeneous. As a result, one must conclude that either the concept of variation of entanglement density with shear rate is inconsistent with the assumptions of the partition model, or else homogeneity does not exist in the non-Newtonian region. The third possibility can be ruled out on the same basis.

As a result, it is concluded that the partition model appears to be consistent with an entanglement concept only for constant entanglement density and reduced entanglement effectiveness as the mechanism for non-Newtonian flow.

Calculation of the MWD from Rheological Data

The calculation of the MWD from rheological data has been reported by various authors. Locata et al.²⁵ use intrinsic viscosity and the zero shear melt viscosity to obtain estimates of \bar{M}_w and \bar{M}_z/\bar{M}_w . However, the method is restricted to log-normal MWD's and polymer systems in which η_0 has a dependence on polydispersity (not just \bar{M}_w). Menefee²⁶ uses stress relaxation data and a modified Rouse based model to calculate the MWD.

It should be possible by inversion of eq. (7) to predict the MWD from data on the steady shear melt viscosity. The inversion of eq. (7) may be effected as follows: Let the index c in eq. (7) be shear-rate dependent. Then, for a specific shear-rate, the viscosity $\eta(\dot{\gamma})$ may be expressed as

$$\eta(\dot{\gamma}_c) = K \left[\sum_{i=1}^{c-1} w_i M_i + M_c \sum_{i=c}^{\infty} w_i \right]^{3.4} \equiv \eta_c \quad (13)$$

or

$$\left[\left(\frac{\eta_{c+1}}{K} \right)^{1/3.4} - \left(\frac{\eta_c}{K} \right)^{1/3.4} \right] = (M_{c+1} - M_c) \sum_{i=c+1}^{\infty} w_i \quad (14)$$

or

$$\sum_{i=c+1}^{\infty} w_i = \frac{\left[\left(\frac{\eta_{c+1}}{K} \right)^{1/3.4} - \left(\frac{\eta_c}{K} \right)^{1/3.4} \right]}{M_{c+1} - M_c} \quad (15)$$

As c increases, $\dot{\gamma}_c$ decreases. By definition, $\sum_{i=c+1}^{\infty} w_i$ is the relative weight percent of the sample above the molecular weight M_{c+1} . In order to reconstruct the MWD, the w_i values corresponding to each molecular weight species are needed. This can be accomplished by noting that

$$\sum_{i=c}^{\infty} w_i - \sum_{i=c+1}^{\infty} w_i = w_c \quad (16)$$

and, therefore,

$$w_c = \left(\frac{1}{K} \right)^{1/3.4} \left[\frac{(\eta_c)^{1/3.4} - (\eta_{c-1})^{1/3.4}}{M_c - M_{c-1}} - \frac{(\eta_{c+1})^{1/3.4} - (\eta_c)^{1/3.4}}{M_{c+1} - M_c} \right] \quad (17)$$

where η_{c-1} , η_c , and η_{c+1} represent the viscosities at closely spaced shear-rate intervals. Consequently, the normalized weight percent of M_c in the sample can be calculated from eq. (17). From w_c and the corresponding M_c calculated from eq. (8) or (9), the entire MWD can be calculated.

The method outlined above has been applied to sample PS-350 described in Table I for the purpose of illustration. The rheological data given in Figure 2 at 225°C were used and the molecular weight distribution averages calculated. The results are given in Table II.

Reasonably good agreement between the averages obtained by means of gel permeation chromatography and those calculated using eq. (17) and rheological data at 225°C is obtained. The absence of a calculated value for \bar{M}_n arises out of the lack of the very high shear-rate rheological data necessary to obtain estimates from eq. (17) of the weight percent of the lower molecular weight homologs.

TABLE II
Comparison of Experimentally Determined and Calculated Molecular Weight Averages of Sample PS-350

	\bar{M}_w	\bar{M}_z
Predicted	310,000	520,000
Experimental (GPC)	290,000	580,000

In fact, eqs. (8) and (9) suggest that information regarding \bar{M}_n is unattainable from rheological measurements of steady shearing flow for broad-MWD samples or for monodisperse samples of very low molecular weight.

ASSESSMENT OF RESULTS IN TERMS OF THE RELATION OF η_0 TO MOLECULAR WEIGHT

Throughout the preceding discussion, specific literature relations of η_0 to molecular weight were employed. However, considering the primary importance ascribed to these relations for relating both viscous and elastic properties to the MWD in the non-Newtonian region, some evaluation of the results in terms of the choice of the η_0 -MWD relation is in order.

Table III contains the experimental and calculated values for η_0 . The η_0 values for the narrow-MWD polystyrenes were obtained from the data of Penwell and Graessley¹¹ by extrapolation and interpolation. A plot of $\log \eta_0$ vs $1/T$ gave approximately straight lines, curving slightly at the higher temperatures. Values for η_0 at 190° and 225°C are shown in the table for both the linear and second-degree polynomial fits. The values of η_0 for the PS-350 were estimated by fitting the data at 190° and 225°C to the Sabia²⁷ model. Besides the relations used in this paper for calculating η_0 from the MWD, calculations of η_0 using an older but widely used relation²⁸ are given. As can be seen from the table, the Zosel⁶ relation gives better agreement with the experimental data used in applying the partition model. While the calculated values of η_0 are not as close to the experimental as one might wish, the agreement is judged satisfactory in light of the rather substantial variations in literature relations.

An error in the zero shear relation can only affect the agreement shown between M_c (as calculated from a broad-MWD sample) and the "onset" on non-Newtonian behavior of "monodisperse" samples by affecting the calculated M_c value at a particular shear rate for the broad-MWD sample. This is true since the molecular weights of the monodisperse materials are independently determined and the absolute values of the viscosities are not used. We have made calculations for PS-350 and determined that by letting K , the constant in the MWD-zero shear relation, vary by 60%, M_c varied by less than 40% over the range of $\dot{\gamma} = 10^{-2}$ to 10^2 sec^{-1} . For a K that is 60% larger than that used by us, α and β , the constants in the relations between the relaxation time and molecular weight

TABLE III

Sample	Method of obtaining η_0	η_0 (190° C), poises	η_0 (225° C), poises
PS-350	Experimental (E)	6.50×10^5	5.98×10^4
	Zosel ⁶ equation (Z)	5.92×10^5	5.92×10^4
	Nielsen ²⁸ equation (N)	9.31×10^5	9.95×10^4
PS-2	E (linear fit)	1.98×10^6	1.26×10^5
	(Polynomial fit)	2.10×10^6	1.77×10^5
	Z	1.94×10^6	1.94×10^5
	N	3.05×10^6	3.26×10^5
PS-1	E (linear fit)	8.32×10^4	3.16×10^3
	(polynomial fit)	1.01×10^5	7.94×10^4
	Z	1.15×10^5	1.15×10^4
	N	1.80×10^5	1.93×10^4

and shear rate, respectively, varied such that α and β were found to be 32×10^{-21} and 2.2. This change in the relation for η_0 changes β from 1.65 to 2.2. Therefore our conclusion as to the apparent agreement between the β for polyethylene and polystyrene at 190°C is relatively insensitive to the choice of relation for η_0 . It should be noted that in order to fit the viscosity data the exponents in eqs. 8 and 9 had to be changed.

Even if there exists a unique relation between η_0 and MWD for a given polymer type, errors involved in the determination of the MWD could be serious to the use of the partition model since \bar{M}_w is being raised to the 3.4th power. As a result, errors in \bar{M}_w will be greatly magnified in calculating η_0 . We believe it is the errors in measuring the MWD that will make agreement between independent investigators difficult. We, therefore, recommend that for a given polymer type, the M_c -vs-shear-rate relation be regarded as relative to the η_0 relation and MWD used. Consequently, in applying our model, an η_0 relation should be chosen that is consistent with the experimental MWD data. After this has been accomplished, the M_c -vs- $\dot{\gamma}$ relation can be determined.

CONCLUSIONS

The ability to predict the rheological curve for an "essentially monodisperse" polystyrene standard, together with the demonstration that M_c values calculated (at given values of the shear rate) from a broad-MWD sample correspond to extremely narrow-MWD polystyrene standards of molecular weight M_c (which are experiencing the onset of non-Newtonian flow at the corresponding shear rates), lends credence to "partition" model assumptions, namely, that (1) the transition from Newtonian to non-Newtonian flow is sharp; (2) M_c , as calculated from polydisperse samples, is indeed the largest molecular weight that can respond in a Newtonian fashion, regardless of polydispersity; and (3) M_c for a given polymer type is a unique function of shear rate, independent of communal properties of the sample as a whole. Further, credence is lent to the model by showing that the temperature dependence of the calculated relaxation spectrum is close to that predicted by the Rouse theory.

The zero shear relation, the material constant α relating relaxation time to molecular weight, and the shear rate dependence of the parameter M_c must be known in order to calculate the viscoelastic functions from the MWD.

The concept of a reduction in entanglement density accounting for non-Newtonian behavior appears to be inconsistent with the assumptions of the model presented here, unless sample homogeneity does not exist under non-Newtonian conditions.

Calculation of the molecular weight distribution from rheological measurements using this model is probably not useful because, unlike the calculation of the rheological flow curve from the complete MWD data, the whole flow curve is impossible to obtain. Certainly, no prediction of \bar{M}_n for broad-MWD samples is possible because the shear rates necessary to obtain the data are unobtainable.

Appendix

The calculation of η/η_0 at the shear rate where $M_c = \bar{M}_w$ can be simplified by noting that any of the MWD's of the anionically polymerized can be approximated by log normal molecular weight

distributions.² From the earlier definition of \bar{M}_w^* , and assuming a log normal molecular weight distribution² which varies continuously with molecular weight, \bar{M}_w^* can be redefined as

$$\bar{M}_w^* = \bar{A}_2 M_c + \frac{\bar{M}_w}{\sqrt{2\pi}} \int_{-\infty}^{\frac{(\sqrt{2} \ln(M_c/M_0)/\beta) - \beta/\sqrt{2}}{\beta}} e^{-z^2/2} dz$$

where

$$\bar{A}_2 = \frac{1}{\sqrt{2\pi}} \int_{\frac{\sqrt{2} \ln(M_c/M_0)/\beta}{\beta}}^{\infty} e^{-z^2/2} dz$$

$$z = \frac{\sqrt{2}(\ln M - \ln M_0)}{\beta}$$

and

$$\beta = [2 \ln(\bar{M}_w/\bar{M}_n)]^{1/2}$$

For $\bar{M}_w/\bar{M}_n = 1.1$ and $M_c = \bar{M}_w$, $\bar{M}_w^* = 0.88\bar{M}_w$ (\bar{M}_w is the actual weight-average molecular weight). Consequently, $\eta/\eta_0 = k[(\bar{M}_w^*)^{3.4}]/k[(\bar{M}_w)^{3.4}] = 0.65$ for $M_c = \bar{M}_w$.

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