An Empirical Model Relating the Molecular Weight Distribution of High-Density Polyethylene to the Shear Dependence of the Steady Shear Melt Viscosity

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Synopsis

An empirical model has been developed to relate molecular weight distribution to the shear dependence of the steady shear viscosity in high-density polyethylene melts. It uses a molecular weight, M_c, which partitions molecular weights into two classes; those below M_c contribute to the viscosity as they do at zero shear, and those above M_c contribute to the viscosity as though they were of molecular weight M_c at zero shear. Each individual molecular weight species contributes on the basis of its weight fraction. M_c is proposed to be a unique function of the shear rate. Using this method of treating the molecular weight distribution, and the zero shear relation for relating η_0 to molecular weight, the calculated steady shear viscosities at various shear rates for polyethylene samples of widely varying polydispersities agree well with experimental results. The model makes no judgment on the existence or importance of entanglements in non-Newtonian behavior since it has no specific parameters involving an entanglement concept. Use of the model suggests that for the samples studied, only the upper portion of the molecular weight distribution contributes toward the experimentally observed decrease of steady shear viscosity with shear rate for shear rates of up to 10,000 sec^{-1}. The lower molecular weight species are assumed to behave in a Newtonian manner.

INTRODUCTION

Numerous theories[1-4] have been advanced to account for the shear dependence of the viscosity in polymer melts and solutions. One of the most successful of these theories is that of Graessley,[1] in which the decrease in viscosity with shear rate is ascribed to a decrease in the entanglement density as a function of shear rate. Graessley assumes a relation between the time necessary for molecular rearrangement (related to the Rouse relaxation time[5]) and the time available (related to shear rate) as molecules move relative to one another. A recent paper[6] has shown that this theory can be applied toward broad molecular weight materials, if the flow curve is somewhat arbitrarily shifted along the shear rate axis to obtain a good fit.

In this paper, a different approach is outlined. Rather than relating relaxation times to the flow curve, molecular weight is related directly to the observed decrease in the steady shear viscosity with shear rate. This approach is shown to account successfully for the non-Newtonian behavior of various high density polyethylene melts of widely varying polydispersities.

EXPERIMENTAL

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

the resulting data. Only data obtained before the onset of unstable flow are reported here.

The gel permeation chromatographic (GPC) data were obtained at 135°C with trichlorobenzene as solvent on a Waters Model 200 instrument having four Styrgel columns of porosities 10^6, 10^5, 10^4, and 10^3 Å. The instrument was calibrated with commercially available polystyrene standards in a modification of the universal calibration procedure. The modifications were judged necessary because of the uncertainty in the Mark-Houwink relation for monodisperse polyethylene fractions and in the uncertain applicability of the universal calibration procedure to the lower molecular weight end of broad-MWD polyethylenes. The modifications involved the linear extension of the universal calibration curve below polystyrene molecular weights of 50,000 and the subsequent empirical generation of self-consistent values for k and a in the Mark-Houwink relation for monodisperse polyethylene fractions by the following procedure.

The k and a values were generated by finding a best fit by means of an iterative procedure for k and a from the following equations:

$$[\eta] = \Sigma W_i[\eta]_i = k\Sigma W_i(M_i)^a$$

and

$$f(V_i) = [\eta]_iM_i = k(M_i)^{1+a}$$

where W_i and M_i are the weight fraction and molecular weight, respectively, of the ith component in the whole polymer; and $f(V_i)$ is the elution volume relation to the hydrodynamic volume $[\eta]_iM_i$ in the universal calibration procedure. This is similar to the procedure of Ram and Miltz[7] used for long-chain branching, except that b and c are constrained to zero. The empirically determined Mark-Houwink relation found from this procedure was $[\eta] = 3.85 \times 10^{-4}M^{0.72}$. This relation is in good agreement with that obtained by the National Bureau of Standards (NBS) using narrow fractions of $[\eta] = 3.92 \times 10^{-4}M^{0.725}$. Using the above Mark-Houwink relation and the universal calibration curve to calculate molecular weight averages for the NBS 1475, good agreement for $\bar{M}_w$ and $\bar{M}_n$ with NBS were obtained, as indicated in Table I.

The linear extrapolation of the universal calibration curve appeared valid because of (1) the good agreement for $\bar{M}_n$ with NBS and (2) the elution volumes for C_{40} (n-tetriacontane) and a 2000 molecular weight linear wax (mo-

TABLE I
Sample Identification

Sample	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_z/\bar{M}_w$
A	204,000	12.2	9.6
B	175,000	11.3	8.8
C	75,000	5.7	5.9
D(NBS 1475 Standard)	56,000(54,200)[a]	2.9(2.96)[a]	3.1
E	157,000	15.9	11.5
F	102,000	13.6	13.6
G	212,000	24.8	9.7

[a] The values in the parentheses are values for $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ obtained by NBS.

lecular weight as determined by vapor pressure osmometry) were in agreement with those predicted by the extrapolated curve.

The high-density polyethylene samples used in this study were selected to represent extremes in molecular weight distributions and were produced by various commercial and experimental processes. The MWD data are given in Table I for these samples.

MODEL DEVELOPMENT

Monodisperse Case

A simplified view of the dependence of the steady shear viscosity on shear rate for monodisperse polymers is depicted by the solid lines in Figure 1. This idealized case is shown in the Appendix to be relatable to the master curves for narrow-MWD polystyrenes by Graessley.[1] Experimentally, the shear rate for the onset of non-Newtonian behavior is not so well defined. The more gradual transition from Newtonian to non-Newtonian flow that is usually found for narrow-MWD polymers is depicted by the dashed line. However, let us assume for the time being that the simplified case represented in Figure 1 adequately approximates the behavior of monodisperse polymers of varying molecular weight.

It has been shown[8] that the zero shear viscosity η_0 is related to molecular weight by $\eta_0 = kM^a$, where $a \simeq 3.36$ for narrow-MWD polyethylene samples having molecular weights exceeding approximately 4000. In view of this relationship the simplified case presented in Figure 1 implies that at any shear rate $\dot\gamma$, there exists a unique value of the molecular weight, M_c, having a zero shear viscosity $(\eta_0)_{M_c}$ such that all molecules having molecular weights M greater than M_c will be undergoing non-Newtonian flow and all samples having molecular weights less than M_c will be in a Newtonian region. Further, from Figure 1,

$$\eta_M = (\eta_0)_{M_c} = kM_c^{3.36} \text{ for all } M \geq M_c > 4000$$

and   (1)

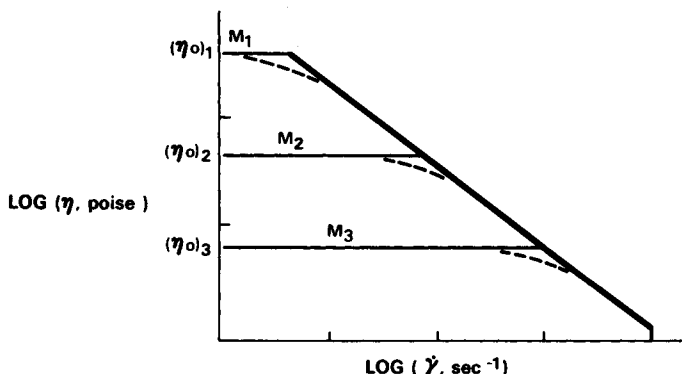$$\eta_M = (\eta_0)_M = kM^{3.36} \text{ for all } 4000 < M < M_c.$$

Fig. 1. Double logarithm plot depicting the idealized relation between the steady shear viscosity η and shear rate for three monodisperse polyethylenes of molecular weights M_1, M_2, and M_3, and zero shear viscosities $(\eta_0)_1$, $(\eta_0)_2$, and $(\eta_0)_3$, respectively, where $M_1 > M_2 > M_3$.

The $(\eta_0)_{M_c}$ will vary with $\dot{\gamma}$, as shown by the heavy line, which is also the power law relation between η and $\dot{\gamma}$ for all $M > M_c$. M_c varies with shear rate as $[(\eta_0)_{M_c}/k]^{1/a}$ varies with $\dot{\gamma}$.

In essence, therefore, M_c acts as movable partition, depending solely on shear rate, that partitions molecular weights into two classes: those acting in a Newtonian fashion for molecular weights below M_c, and those undergoing non-Newtonian flow and giving a viscosity equivalent to a zero shear viscosity of a lower molecular weight material having a zero shear viscosity $(\eta_0)_{M_c}$.

Polydisperse Case

To calculate the steady shear viscosity at any shear rate for broad-MWD polymers, the relation between zero shear viscosity and molecular weight will be assumed to be known, adequately accounted for by current theories, and valid for any nonzero shear rate. An empirical relationship for polyethylene at 190°C reported[8] in the literature will be used:

$$\log \eta_0 = -12.296 + 3.36 \log \overline{M}_w + 0.51 \log (\overline{M}_z/\overline{M}_w). \tag{2}$$

This relationship, which is quite close to theories[9,10] predicting the variation of η_0 with the 3.4 power of $\overline{M}_w$ for narrow fractions, was obtained using both fractions and polydisperse linear polyethylenes.

As with the monodisperse materials already discussed, there will be assumed to exist at any shear rate a maximum molecular weight M_c, below which molecules contribute to the viscosity as they normally would. For $M \geq M_c$, a molecule will contribute to the viscosity in proportion to its weight fraction as though its molecular weight were M_c. This partition will be assumed to be independent of the molecular weight or the MWD of the sample as a whole. Consequently, the steady shear viscosity at any shear rate can be expressed as

$$\log \eta_0 = -12.296 + 3.36 \log \overline{M}_w{}^* + 0.51 \log [(\overline{M}_z)^*/(\overline{M}_w)^*]. \tag{3}$$

where

$$(\overline{M}_w)^* = \sum_{i-1}^{i=c-1} w_i M_i + M_c \sum_{i=c}^{i=\infty} w_i,$$

$$(\overline{M}_z)^* = \sum_{i-1}^{i=c-1} w_i M_i^2 + M_c^2 \sum_{i=c}^{\infty} w_i \bigg/ \sum_{i-1}^{i=c-1} w_i M_i + M_c \sum_{i=1}^{\infty} w_i$$

and w_i is the weight fraction of the ith component. In terms of the GPC data, the MWD is split into a histogram with rectangles of width ΔV_i, of $\frac{1}{10}$ count. As a result, w_i as defined above is equivalent to

$$h_i \cdot \Delta V_i / \sum_{i=1}^{\infty} h_i \cdot \Delta V_i$$

where h_i is the peak height of the ith rectangle and ΔV_i is the elution volume increment; M_i is determined from the universal calibration curve at the elution volume V_i. From the experimental relation of η versus $\dot{\gamma}$ and MWD
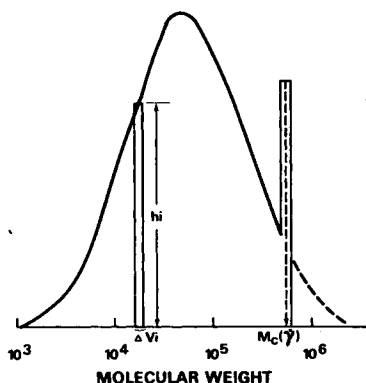
Fig. 2. The effective molecular weight distribution at $\dot{\gamma}$ is depicted by the solid line, where M_c is the partitioning molecular weight at $\dot{\gamma}$. The dashed portion of the curve shows the actual high molecular weight portion of the molecular weight distribution as measured by gel permeation chromatography.

data, eq. (3) is solved for M_c as a function of $\dot{\gamma}$ by the use of an interval halving computer program.

In effect, this model assumes the validity of the zero shear relation between viscosity and molecular weight, except that at nonzero shear rates an effective MWD as defined by the partition functions given above is used. An example of a modified MWD is illustrated in Figure 2. This application of characteristics of monodisperse materials to the polydisperse case has been used by Middleman,[2] although the basic assumptions appear to be quite different.

RESULTS AND DISCUSSION

Three criteria are used to judge the success of the assumptions of applying the approximate relations for monodisperse samples to polydisperse materials. First, and most important, samples of varying MWD's should give the same relationship of M_c to $\dot{\gamma}$. Second, it should be possible to use the empirical relationship of M_c with $\dot{\gamma}$ to obtain the approximate power law relation,[11] $\eta \simeq A\dot{\gamma}^{-0.80}$, through the relation $\eta = kM_c^{3.36}$ (i.e., since for monodisperse materials, the power law relation is interpreted as just the variation of $M_c^{3.36}$ with $\dot{\gamma}$). Third, the molecular weight dependence of the longest relaxation time should be able to be predicted from the model.

Prediction of Steady Shear Viscosity

Figure 3 contains the results of the calculation of M_c from both the rheology and GPC data for samples A through D, which represent widely varying polydispersities. The relations between M_c and $\dot{\gamma}$ for the four samples appear to be in very good agreement, especially considering the application of a specific literature relationship of melt viscosity to the molecular weight data given here. Consequently, we shall consider the line drawn in Figure 3 to be applicable for any linear polyethylene regardless of polydispersity.

Figures 4a and 4b show the predicted and experimental viscosities as a function of shear rate for samples A through D. The predicted viscosities were obtained by using M_c (as obtained from Fig. 3) and the experimental
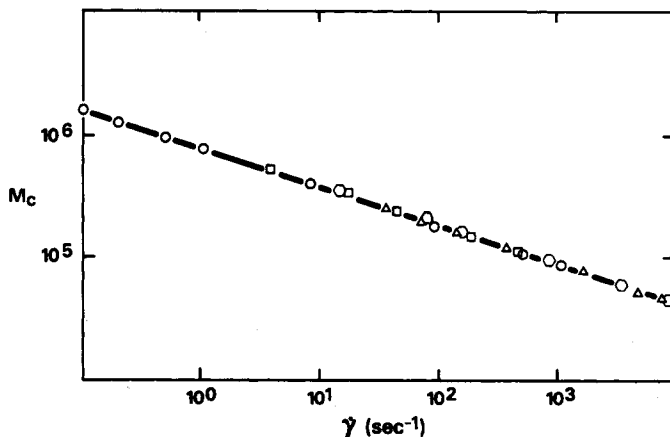
Fig. 3. Plot of the calculated critical molecular weight M_c vs. shear rate for samples A (□), B (O), C (◯), and D (△).

MWD data to predict the viscosity from eq. (3). By use of this method, the melt viscosity of any HDPE sample should be predictable at any shear rate from the MWD data alone.

Figures 4c and 4d contain experimental and predicted data on HDPE samples E through G. Again, the agreement between the predicted and experimental viscosities appears to be quite good for all the samples, even though Figure 3 was obtained from samples A through D, which have vastly different MWD's from samples E through G. It is regrettable that lower shear rate data using a cone-and-plate viscometer were not available. However, because an experimentally determined relationship between zero shear viscosity and molecular weight was used as a starting point, the extremely low shear rate application of the relationship should be the most reliable.
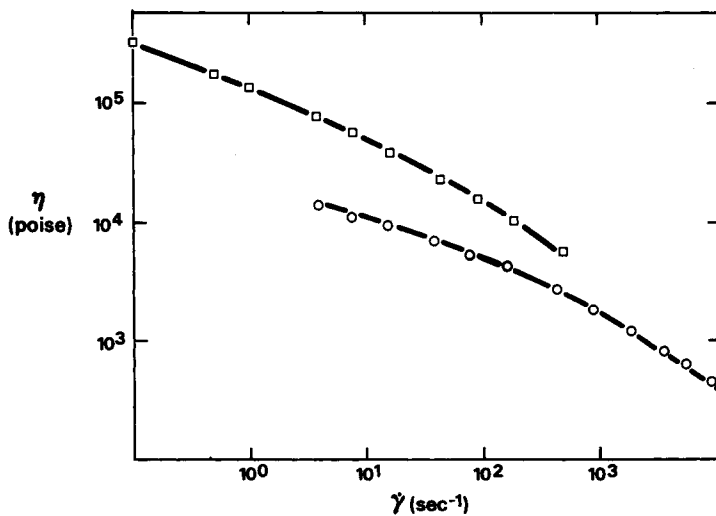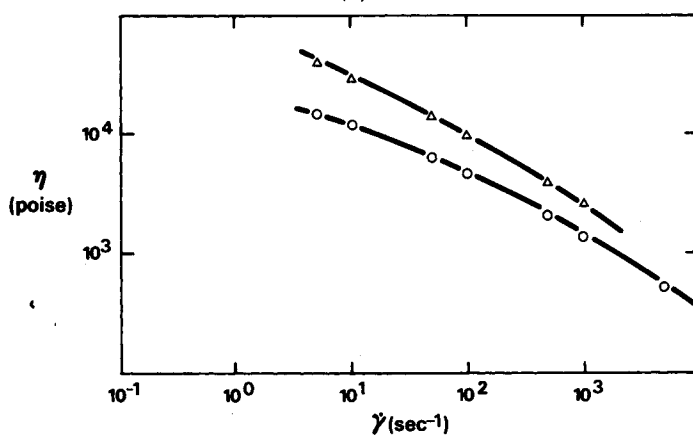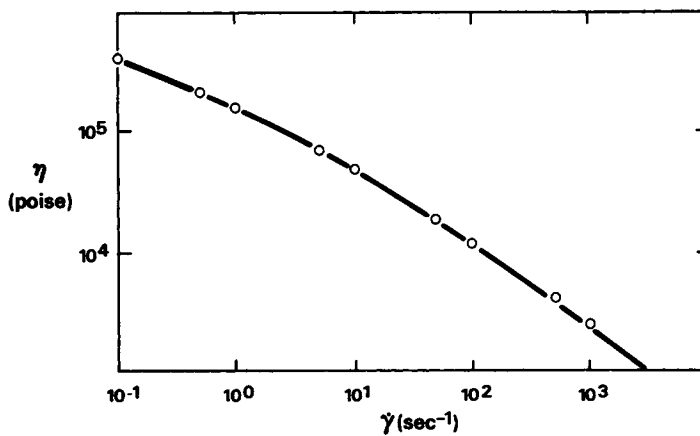

(a)

Fig. 4. continued
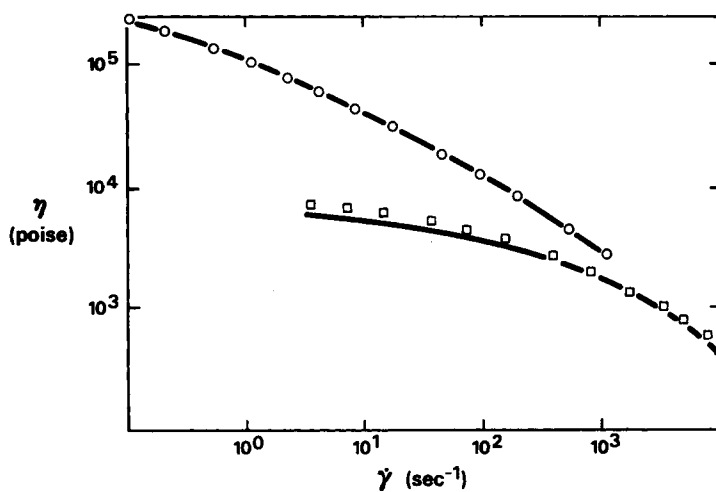
(b)

(c)

(d)

Fig. 4. Apparent viscosity η as a function of shear rate. The experimental curves are depicted by the solid lines and the calculated values for η are given by the □'s, O's, △'s; (a) Sample A (□) and Sample C (O); (b) Sample B (O) and Sample D (□); (c) Sample E (△) and Sample F (O); (d) Sample G (O).

This model also offers some insight into just what part of the MWD contributes to the observed change of viscosity with shear rate. Figure 3 indicates that molecular weights up to 40,000 are still apparently in a Newtonian region at 10,000 sec^{-1}. Consequently, from Figure 2, it is seen that the functional decrease of η with shear rate up to 10,000 sec^{-1} has been governed almost completely by the upper portion of the MWD; the lower portion of the MWD contributing mainly through the weight fraction term as a diluent. This conclusion was found to be valid for samples A through G from a consideration of the MWD curves.

Prediction of the Onset of Non-Newtonian Flow

The "partition" model presented here predicts that the viscosity will be Newtonian at shear rates such that the largest molecular weight species does not exceed M_c. By extrapolating the relation given in Figure 3 to lower shear rates, and noting the largest observable molecular weight present in the MWD from GPC, the shear rate for the onset of non-Newtonian flow can be predicted. This has been done and the results are given in Table II, together with the values as estimated from rheological data. The estimated onset of non-Newtonian flow from rheological data was obtained using the extrapolation procedure of Spencer and Dillon.[12] As can be seen from Table II, the results are surprisingly good considering the extrapolation used for the rheology data. However, the extrapolation in the case of the NBS 1475 sample is probably the most accurate since the extrapolation involves an extrapolation less than one decade in shear rate.

The Power Law Relationship

This model implies that the power law region is just the variation of M_c to the a power (i.e., η/k) with $\dot\gamma$ for a sample in which all molecular weights exceed M_c. However, the plots in Figures 2 and 3 show that the true power law region is not predicted for all but the narrowest MWD's; some molecules in a broad-MWD material are still smaller than M_c at shear rates as large as 10,000 sec^{-1}, and they are consequently not following the predetermined decrease in viscosity that molecules larger than M_c are. From the slope in Figure 3 and eq. (1), the exponent in the power law relation between η and $\dot\gamma$ is calculated to be -1.055 when the smallest molecular weight in a sample is

TABLE II
Estimated Versus Calculated Shear Rate for the Onset of Non-Newtonian Flow

Sample	Predicted shear rate for the onset of non-Newtonian flow from molecular weight distribution, sec^{-1}	Estimated shear rate for the onset of non-Newtonian flow from extrapolation of rheological data, sec^{-1}
A	2×10^{-4}	1×10^{-4}
B	1×10^{-3}	3×10^{-3}
D(NBS 1475 Standard)	4×10^{-1}	5×10^{-1}

larger than M_c. This calculated value for the exponent is within experimental error the same as the theoretical limit of -1.0, although this limit is probably experimentally unattainable. The idea of a limiting value of -1.0 for the power law exponent, in which the shear stress approaches a constant value, is in agreement with that predicted from the theory of Williams[13] for monodisperse concentrated solutions. However, this exponent is significantly less than the value of -0.80 as experimentally reported by Sabia[11] and that of -0.818 predicted by Graessley's theory.[1]

A possibility which might account for the predicted power law exponents being larger than that experimentally observed is the crudeness of the assumption made from Figure 1 that the transition from Newtonian to non-Newtonian behavior is sharp for a monodisperse sample. For the case of a gradual transition, the viscosity contribution of a molecule in the transition region would be less than that predicted for the sharp transition illustrated in Figure 1. As a result, the calculated values of M_c would tend to be larger at the high shear rates, where a proportionately larger weight fraction of molecules are affected resulting in a smaller predicted dependence of η on $\dot{\gamma}$ in the power law region would result. However, the quantitative effect on the power law exponent of substituting a gradual transition into the present model is not immediately apparent.

Molecular Relaxation Times

This model does not contain any explicit reference to molecular relaxations as do models duch as those of Rouse[5] or Graessley.[1] However, the assumption of an upper limit to the effective molecular weight M_c as a function of shear rate in the present model can be rationalized in terms of molecular relaxations. The partitioning of the MWD into molecular weights that act in a Newtonian fashion and those that do not implies that the non-Newtonian group can no longer respond (or relax) within the time scale of the experiment (i.e., $\sim k/\dot{\gamma}$). Consequently, the partitioning molecular weight M_c is the highest molecular weight which can completely relax in the time allowed at a given shear rate. If it is assumed that the maximum allowed relaxation time is proportional to $1/\dot{\gamma}$, then it follows from Figures 1 and 3 that (1) the maximum relaxation time allowed determines the effective molecular weight of molecules larger than M_c, independent of the molecular weight or viscosity of the sample as a whole, and (2) the maximum allowed relaxation time at $\dot{\gamma}$ will be proportional to $M_c{}^{3.19}$. From the definition of M_c as the largest molecular weight that can still relax fully at $\dot{\gamma}$, the maximum allowed relaxation time, $k/\dot{\gamma}$, corresponding to M_c in Figure 3, is just the maximum relaxation time of a molecule of molecular weight M_c. More generally, the maximum relaxation time for a molecule of molecular weight M is proportional to $1/\dot{\gamma}$ or, from Figure 3, proportional to $M^{3.19}$. This is in reasonable agreement with published[14] experimental results for the relation between maximum relaxation time and the molecular weight of narrow-MWD melts and solutions where the 3.4 power relation is found.

In contrast to this model, Graessley's theory assumes that at any shear rate, the maximum relaxation time is proportional to η, which is a characteristic of the sample as a whole. However, because this model treats the sum-

mation of individual molecular responses rather than the response of the assemblage as a whole, the differences are somewhat hard to evaluate.

Molecular Entanglements

It is pertinent to note that the model presented here contains no parameters which directly relate to an entanglement factor. Although the treatment presented here neither proves nor disproves the concept of entanglements being the origin of non-Newtonian behavior, speculation regarding the physical meaning of my "partition" model in terms of the entanglement model may be helpful.

In the model presented here, M_c is defined as the largest molecular weight that can undergo Newtonian flow at $\dot{\gamma}$. In terms of the entanglement model, in which non-Newtonian flow is attributed to the inability to fully reentangle to an equilibrium situation, M_c represents the largest molecule that can fully reentangle at a particular shear rate. Molecules larger than M_c still reentangle, but to a reduced degree depending on the shear rate. These long molecules exhibit reduced drag forces due to the reduced entanglement densities.

While the preceding rationalization of the "partition" model in terms of the prevailing entanglement concept gives a plausible mechanism, more experimental data on other polymer systems are needed to more fully test and develop the present model.

CONCLUSIONS

The model presented here successfully predicts the observed non-Newtonian decrease in steady shear viscosity with shear rate and the molecular weight dependence of the maximum relaxation time for a series of high-density polyethylene samples of varied molecular weight distributions.

No definitive judgment can be made from the model regarding the existence or importance of entanglements in non-Newtonian flow since the generality of the model precludes the precise assignment of mechanism. However, the presented model may disagree with one aspect of the entanglement theory of Graessley in that the model indicates that the longest relaxation time allowed at any given shear rate is dependent only on a given molecule's molecular weight, not on cummunal properties of the sample as a whole such as the sample viscosity. The maximum molecular relaxation time is predicted to be proportional to the 3.19 power of molecular weight.

The presented model demonstrates that only the upper portion of the MWD contributes toward the experimentally observed non-Newtonian steady shearing flow for broad-MWD high-density polyethylene samples.

Appendix

The observation by Graessley[1] that a master flow curve for narrow-MWD polystyrenes can be formed using as variables η/η_0 and $\dot{\gamma}\tau_0/2$ may be shown to be an approximate restatement of Figure 1 from the following argument. From the master plot of Graessley, the following relation was found to hold

for any molecular weight sample undergoing non-Newtonian flow (assuming an infinitely sharp non-Newtonian transition):

$$\log\eta - \log\eta_0 = a \log\dot\gamma + a \log\tau_0 + \text{constant} \quad (4)$$

where a was approximately -0.75 and τ_0 approximately proportional to $\eta_0 M$ (M is the molecular weight and η_0 the zero shear viscosity). Assuming η_0 is proportional to $M^{3.4}$, we obtain the relation

$$\log\eta \approx -.75 \log\dot\gamma + \text{constant}. \quad (5)$$

This means that, at shear rates above those where non-Newtonian flow begins for monodisperse samples of varying molecular weights, these samples will have flow curves in the power law region that are virtually superimposible (i.e., the heavy solid line in Fig. 1).

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