

Prediction of Rheological Behavior of Branched Polyethylene from Molecular Structure

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Synopsis

The general description of steady shear melt viscosity as a function of shear rate for polyethylene, containing any level of long chain branching, in terms of molecular structure is reported. A model, developed previously by B. H. Bersted for the prediction of rheological properties from the molecular structure of linear materials, and which has been subsequently modified by Ram and Pedersen for application to highly branched low-density polyethylene, is extended to describe the flow behavior of branched high-density polyethylene. The description of the branched high-density polyethylenes, which characteristically show dramatic viscosity enhancement relative to linear polyethylene, is effected by considering these materials to be blends of branched and linear species. A logarithmic rule of mixtures was found adequate at all shear rates for the description of blends of branched and linear materials.

INTRODUCTION

Long chain branching (LCB) can produce very dramatic changes in rheological behavior.¹ Perhaps the most well-documented example of the effect of LCB for commercial materials is afforded from the comparison² of the rheological behavior of low-density polyethylene (LDPE, as produced by the high-pressure free-radical process) and linear high-density polyethylene (HDPE). In general, the LDPE materials have greatly diminished melt viscosities relative to the linear HDPE at constant weight average molecular weight (\bar{M}_w). These differences lead to quite different processing capabilities and uses for HDPE and LDPE.

These rather simple generalizations, however, seem to break down when LCB is present at low concentrations and for high molecular weights.¹ In this latter case, dramatic viscosity enhancement at low shear rates has been observed.¹⁻³ Certain HDPE materials display this rather bizarre rheological behavior, which appears to be characteristic of neither the highly branched LDPE nor the linear HDPE materials. The strikingly different rheological behavior for two HDPE samples of similar \bar{M}_w is shown in Figure 1. It is the purpose of this article to demonstrate that the rheological behavior of these materials, showing viscosity enhancement and containing very small amounts of LCB, can be adequately described by treating the material as a blend of branched and linear polyethylene. This description will make use of a combination of equations developed for highly branched LDPE samples and those developed previously⁴ for linear HDPE.

In the past couple of years, we have proposed⁴⁻⁸ a model to describe the rheological behavior of linear HDPE in terms of the molecular weight distribution (MWD). This model has more recently been extended by Ram and Pedersen⁹ for application to LDPE. The extension of the model involved replacing the

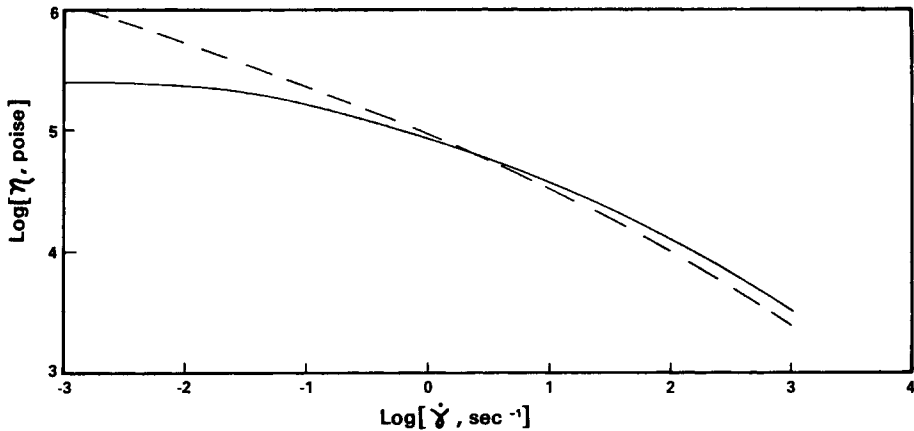


Fig. 1. Typical flow curves for branched (sample B, --) and linear HDPE (sample F, —).

molecular weight by the mean square radius of gyration in the more general case. We will show in this article that this more general case can account for the rheological behavior of even materials demonstrating viscosity enhancement, if the material showing the enhancement (HDPE) is regarded as being composed of linear and branched components.

MODEL DESCRIPTION

The model developed by Bersted⁵⁻⁸ has been shown to be capable of describing the steady shear viscosity, first normal stress difference, dynamic small strain, stress overshoot, and extensional behavior¹⁰ of linear HDPE and polystyrene melts in terms of the distribution of chain lengths. For the description of the steady shear viscosity it is assumed that the viscosity at any shear rate can be described by

$$\text{Log } \eta(\dot{\gamma}) = A \log (\bar{M}_w^*) + b \log (\bar{M}_z^*/\bar{M}_w^*) + \log K \quad (1)$$

where

$$\bar{M}_w^* = \sum_{i=1}^{c-1} w_i M_i + M_c \sum_{i=c}^{\infty} w_i$$

and

$$\frac{\bar{M}_z^*}{\bar{M}_w^*} = \frac{\sum_{i=1}^{c-1} w_i M_i^2 + (M_c)^2 \sum_{i=c}^{\infty} w_i}{\bar{M}_w^*}$$

$M_c(\dot{\gamma})$ is a shear rate parameter that partitions molecular weights into two classes: molecular weights below M_c contribute to the viscosity as at zero shear rate and those greater than M_c contribute to the viscosity as though they were of molecular weight M_c . K and A are the usual constants in the zero shear relationship. For the case of HDPE, A was taken as 3.36, K was 3.16×10^{-13} , and b was 0.51:

$$\text{Log } (M_c) = 5.929 - 0.290 \log \dot{\gamma} \quad (2)$$

The extension of this model to low-density polyethylene was reported by Ram and Pedersen⁹ by the use of the distribution of the mean square radius of gyration instead of the molecular weight. The mean square radius of gyration being proportional to gM , where g is by definition the ratio of the mean square radius of gyration for a branched to linear molecule of identical molecular weight.

The relationship in eq. (1) is based on the assumption that each individual species of differing molecular weight contribute to the viscosity in a fashion proportional to its weight fraction and whether its molecular weight exceeds M_c . $M_c(\dot{\gamma})$ is defined to be the largest molecular weight species contributing as though it were Newtonian at $\dot{\gamma}$.

EXPERIMENTAL

The samples studied here are various commercial and experimental polyethylene resins. Molecular structure information on these materials is summarized in Table I.

The gel permeation chromatographic (GPC) data were obtained at 135°C with trichlorobenzene as solvent using a Waters model 200 instrument. The instrument was calibrated by means of a modified universal calibration procedure. The determination of LCB was made using the procedure of Ram and Miltz.¹¹ One important difference in their procedure was instituted. The constant, K , for the Mark-Houwink relationship between molecular weight and intrinsic viscosity was determined in such a way that a group of linear HDPE samples (including the National Bureau of Standards NBS-1475) were predicted to be linear by the Ram and Miltz¹¹ procedure. We feel this "linear calibration" is necessary in the determination of low levels of LCB. Our final values for the Mark-Houwink constants were $K = 5.38 \times 10^{-4}$ dl/g and $a = 0.700$.

The GPC data for samples B and F were replicated in order to confirm that differences in their MWDs were in fact significant. Thus, while the estimated 2σ for \bar{M}_w is approximately 10%, the mean values of the replicate runs for these samples are considered to be known with greater certainty.

The intrinsic viscosity data, which is necessary to obtain molecular structure data corrected for branching determination by means of the method of Ram and Miltz, were obtained using trichlorobenzene as a solvent at 135°C. The Ram and Miltz¹¹ technique for branching yields the ratio of the intrinsic viscosity (for each molecular species i in the sample) of the branched and linear species of identical molecular weight. These ratios were equated to $(g_i)^{1/2}$, where g_i is the ratio of the mean square radius of gyration for a branched to linear molecule of

TABLE I
Molecular Parameters of Polyethylene Samples

Sample	LCB/1000CH ₂ units	X10 ⁻³					
		\bar{M}_n	\bar{M}_w	\bar{M}_z	$(g\bar{M})_n$	$(g\bar{M})_w$	$(g\bar{M})_z$
A	0	8.4	91	378			
B	0.05	11.3	157	1150	11.2	141	932
C	1.21	18.2	176	936	15.2	38.5	62.4
D	1.68	18.0	95.2	378	14.1	25.6	36.1
E	1.17	20.6	192	1634	16.9	42.5	68.2
F	0	10.9	161	1070			

identical molecular weight. The number of branches per chain were then calculated for each species comprising the whole sample from the Zimm-Stockmayer relationship¹² for a monodisperse sample containing random trifunctional branch points. The average number of LCBs per 1000 CH₂ units was calculated from

$$\langle \text{Number LCBs/1000 CH}_2 \rangle = 14,000 \sum w_i n_i / M_i$$

where w_i is the weight fraction of the i th component, n_i the number of branches per molecule for the i th component, and M_i the corrected (for branching) molecular weight of this component.

The melt viscosity data were obtained at 190°C. The high shear rate data were obtained using an Instron capillary rheometer with a capillary having an L/D of 33:1. Low shear data were obtained either using a Weissenberg rheogoniometer with a cone and plate configuration (radius 1.25 cm, cone angle 0.07 rad) or using a melt flow indexer as described by Ram and Miltz.¹³ Newtonian viscosities were estimated using the Cross equation for extrapolation.

RESULTS AND DISCUSSION

Application of Linear Model to HDPE Containing Little LCB

Sample B in Table I is typical of HDPE resins containing extremely small degrees of LCB. It is the description of the rheological behavior of this type of material in terms of molecular parameters that is the goal of this article. Since the degree of branching is quite small, the corrections to the molecular weight distribution are correspondingly small. As a result, the search for an adequate description suggests that we compare the predictions of eqs. (1) and (2), which have previously been found⁴ to describe successfully the flow curves from MWD data for linear polyethylene resins. Comparison of the predicted curve with experimental data for sample B and with a linear HDPE of comparable molecular weight, may be made from reference to Figure 2. As can be seen from the figure, the experimental data shows dramatic viscosity enhancement at the lowest shear rates and a somewhat diminished viscosity at the highest shear rates relative to the predictions based on equations found useful for linear HDPE. It is obvious from this comparison that the branching, even though it is present at extremely low levels, must radically change the flow mechanism and must be taken into account. The description of the rheological behavior of a type of resins like sample B is of great practical interest, since the large rheological differences relative to linear materials give these resins certain advantages in commercial processes such as blow molding, in which a high low-shear-rate viscosity and a low high-shear-rate viscosity are desirable.

Development and Application of a Branched Model

In view of the poor agreement of the experimental data and predictions based on the treatment of the branched HDPE materials as linear, the effects of branching must be taken into account. In this section, the applicability of a model developed for low-density polyethylenes will be discussed.

Ram and Pedersen⁹ have recently demonstrated that the model of Bersted⁴⁻⁸

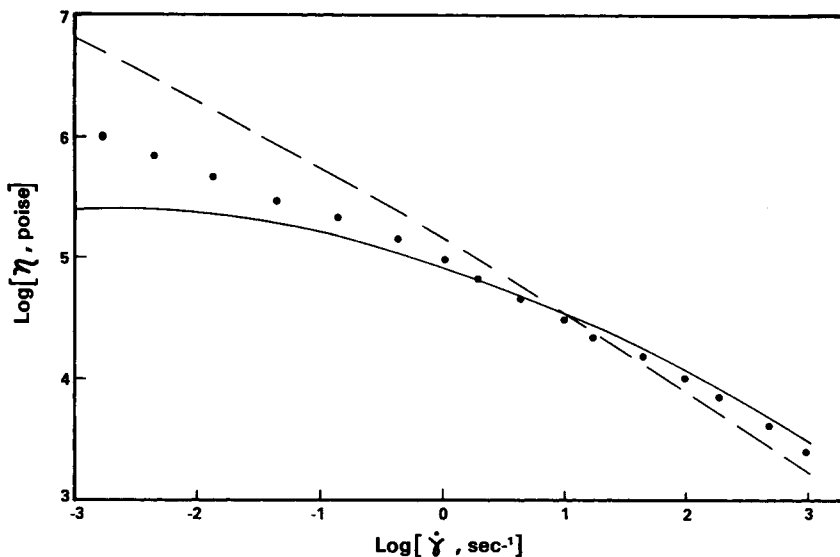


Fig. 2. Comparison of predictions based on branched (---) and linear (—) models with experimental data (●) for sample B.

can be generalized quite simply by using the distribution of the unperturbed mean-square radius of gyration \overline{S}_o^2 instead of the molecular weight distribution. \overline{S}_o^2 is proportional to the molecular weight ($g \equiv 1$) for linear materials and proportional to gM for branched materials, g being the ratio of \overline{S}_o^2 for the branched to linear value at equivalent molecular weights.

Following Ram and Pedersen,⁹ we first determine the relationship between $(g\overline{M})_w$ (the weight average of gM) and the Newtonian viscosity, η_o , for a selected group of LDPE samples. The resulting data are plotted in Figure 3. A least-squares fit to the data produced the following relation between $(g\overline{M})_w$ and η_o :

$$\log(\eta_o) = -30.18(\pm 3.25) + 7.9(\pm 0.74) \log(g\overline{M})_w$$

The value of 7.9 arrived at here is considerably more than that of 4.28 reported by Ram and Pedersen.⁹ However, it is in significantly better agreement with the values of 6.56 and 8 reported by Mendelson, Bowles, and Finger³ and Wales,¹⁴ respectively. In a similar fashion to that described previously,⁴ the parameter $(gM)_c$, which satisfied the following equation, was determined as a function of shear rate.

$$\log \eta(\dot{\gamma}) = -30.18 + 7.9 \log(g\overline{M})_{w^*} \quad (3)$$

where

$$(g\overline{M})_{w^*} = \sum_{i=1}^{c-1} w_i (gM)_i + (gM)_c \sum_{i=c}^{\infty} w_i$$

and w_i the weight fraction of the i th component. $(gM)_c$ as a function of shear rate was determined to be

$$\log(gM)_c = 4.67 - 0.112 \log \dot{\gamma} \quad (4)$$

Figures 4 and 5 demonstrate the ability of eqs. (3) and (4) to describe the viscosities as a function of shear rate for samples D and E.

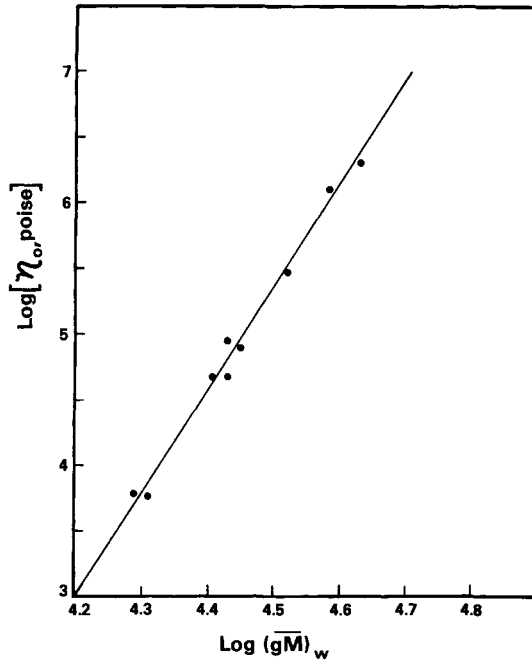


Fig. 3. Zero shear viscosity as function of weight average of radius of gyration.

Comparison of the predictions, using these equations, the distribution of gM , and the experimental data for sample B is made in Figure 2. Poor agreement of the predictions with the experimental data is evident from the figure at low shear rates. Interestingly, however, the disagreements in Figure 2, between the branched predictions and the experimental data, are essentially the reverse of those in which the sample was treated as linear. In fact, the experimental data appear as though it could be a combination of the linear and branched cases. As will be demonstrated later, this supposition appears to provide a satisfactory description.

The reason why neither treating the sample as linear or as branched gives

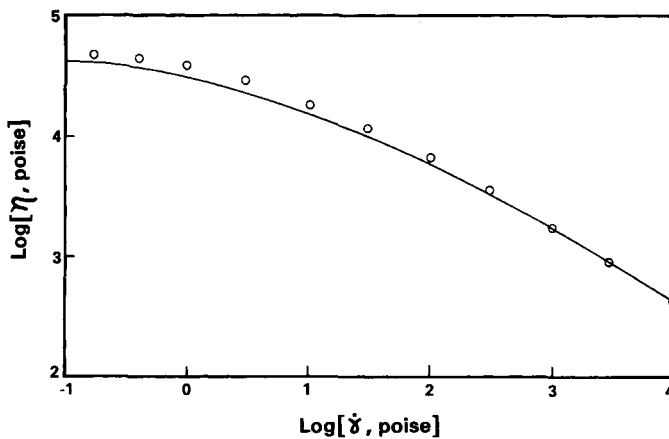


Fig. 4. Comparison of predicted (O) and experimental (—) flow curves for sample D.

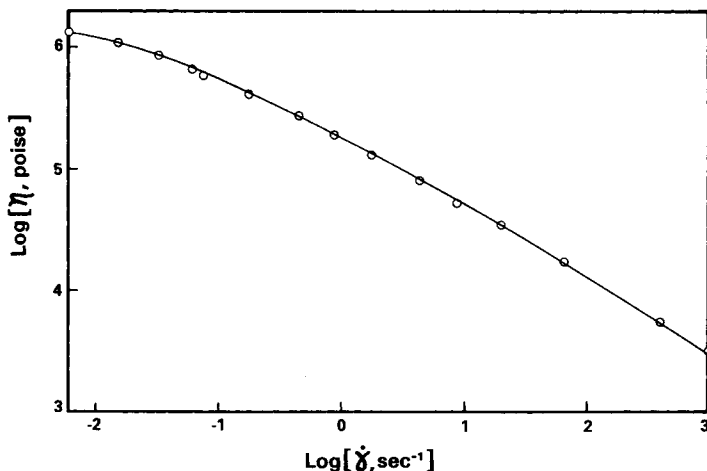


Fig. 5. Comparison of predicted (O) and experimental (—) flow curves for sample E.

predictions in agreement with the experimental data, and why the experimental data appears to be a combination of the linear and branched predictions, can be understood in terms of the low level of LCB present in sample B. The weight-average number of LCBs per molecule for this sample is 0.63, implying that a substantial fraction of the molecules must be linear. The next sections quantitatively explore the ramifications of regarding this sample as a blend of branched and linear species. The application of the Bersted model to this case is not intuitively obvious, since the different species are described by different zero shear relationships and different shear dependencies of M_c and $(gM)_c$.

Development of Relationships for Blends of Branched and Linear Components

As stated earlier, the description of the rheological behavior of a blend of linear and branched components, both of which are characterized by quite different relationships between rheological behavior and molecular structure, in terms of the components is not immediately evident. Blends of a HDPE (sample A) and a branched LDPE (sample C) were produced by solution blending, in order to attempt to find a relationship between the rheology of the blend and the rheology of the components.

The correlation between Newtonian viscosity of the blend and the blend composition is shown in Figure 6. This figure suggests the following relationship:

$$\eta_o(\text{blend}) = (\eta_{oL})^{w_L}(\eta_{oB})^{w_B} \quad (5)$$

where w_L and w_B are the weight fractions of the linear and branched component, respectively. This relation is consistent with the linear additivity of the activation energies for blends of HDPE and LDPE reported by Porter, Jacowic, and Pollock.¹⁵

One of the fundamental assumptions of the Bersted model is the independence of the shear rate effects of the various molecular species. We would, therefore, expect eq. (5) to be generalized to

$$\eta(\dot{\gamma}, \text{blend}) = [\eta_L(\dot{\gamma})]^{w_L}[\eta_B(\dot{\gamma})]^{w_B} \quad (6)$$

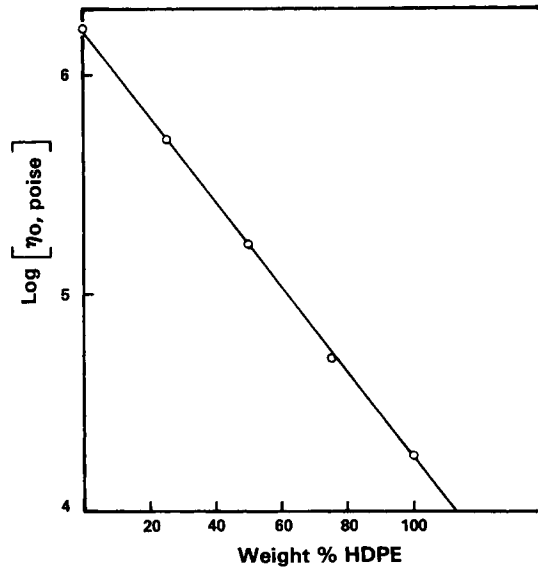


Fig. 6. Zero shear viscosity as function of blend composition for blends of HDPE and LDPE (samples A and C).

This relationship is conclusively shown to be applicable from reference to Figures 7 and 8.

The use of two completely different relationships for the branched and linear species in eq. (6) for describing the behavior of molecules of a sample presumed to be structurally homogeneous appears improper at first glance. However, one of the fundamental assumptions of the Bersted model, as given in eq. (1), is the

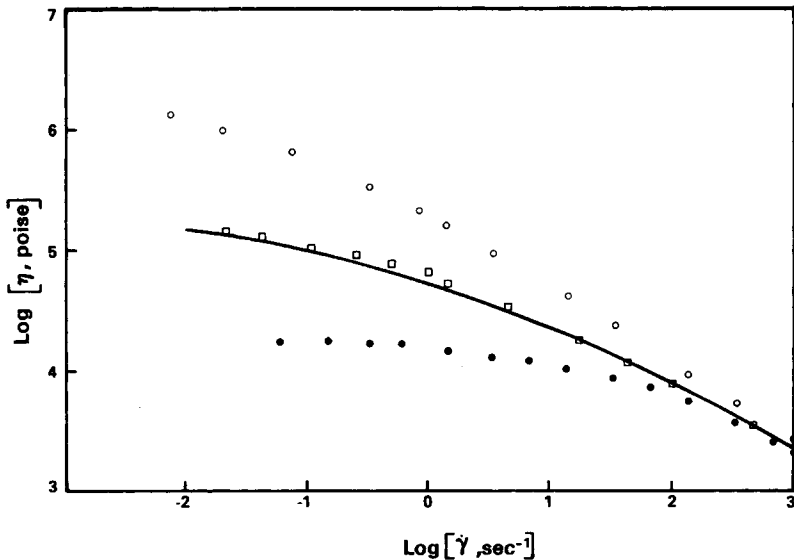


Fig. 7. Flow curves of blend components and 50/50 blend; O, sample C; ●, sample A; □, 50/50 blend of A and C; —, predicted flow curve based on eq. (6), experimental data for samples A and C.

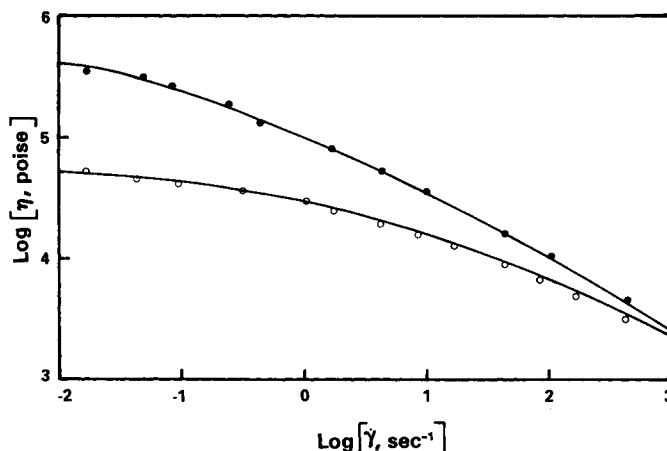


Fig. 8. Comparison of experimental and predicted (—) flow curves for blends of samples A and C; ●, 75/25 blend of sample C/sample A; ○, 25/75 blend of sample C/sample A.

independence of the contributions of the individual molecular components in the sample.

Treatment of Branched HDPE as Blend of Linear and Branched Components

We are now in a position, based on eqs. (1)–(4) and (6), to compare the predicted flow curve with that experimentally observed. However, the values used for w_L and w_B will have to be scrutinized for the following reason. If, for example, we have an average of one long chain branch per molecule, then, because of the very different relationships between viscosity and molecular structure for branched and linear materials, it makes a substantial difference in the rheological predictions if the average represents all molecules having one branch or if the sample is composed of some molecules possessing two branches and the same number being linear. Arguments based on the assumption of random branching are presented in Appendix A giving w_L and w_B in terms of the average branch content. For the case of sample B, w_L and w_B are calculated as from Appendix A to be 0.18 and 0.82, respectively. Calculating the flow curve for the linear case from eqs. (1) and (2), calculating the flow curve for the branched case from eqs. (3) and (4), and using eq. (6) with $w_L = 0.18$ and $w_B = 0.82$, the predicted flow curve for the postulated blend can be calculated. The predicted flow curve is compared with the experimental data in Figure 9. The very good agreement shown in Figure 9 is gratifying in view of the apparent complexity of this class of materials. It is also interesting to note that the mixing relationship in eq. (6) appears to be entirely consistent with the spirit of the Bersted⁴ model, since it also implies independence of the Newtonian–non-Newtonian behavior of the various molecular species present in a polydisperse sample.

It is interesting to contrast the ideas reported here with the data of Graessley, Raju, and Rachapudy¹⁶ for three- and four-arm star hydrogenated polybutadienes. The major difference between the samples studied here and those of Graessley et al. is the expected distribution of LCB. For the samples studied here, branching would be expected (at least to a first approximation) to be a

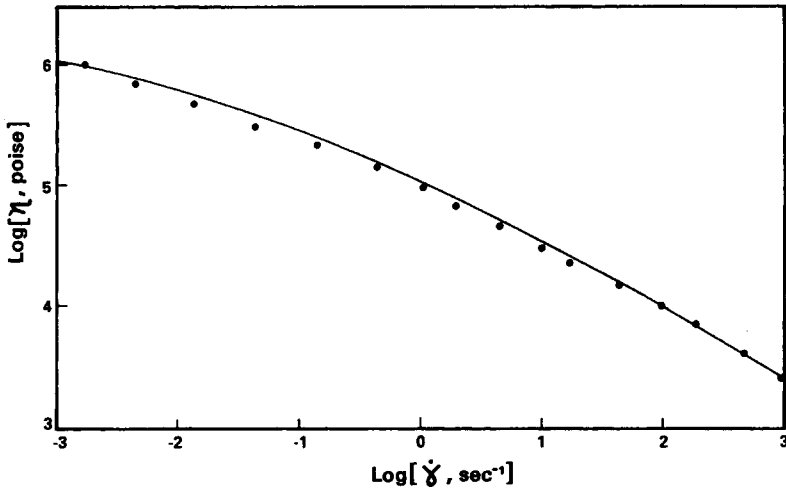


Fig. 9. Experimental (●) and predicted (—) flow curve for sample B using blend model.

random process, with the result that at low levels of branching not every molecule would contain a branch. However, owing to the method of preparation, the samples of Graessley et al. are uniformly branched, even at the low levels discussed for sample B in this article. The data of Graessley et al. suggest that the viscosity enhancement of the branched species depends on branch length. However, our analysis predicts enhancement either from (a) an increased concentration of branched species or (b) from increased gM , depending on whether the enhancement is approached by changing the branching level from the linear or highly branched states. There would appear to be no contradiction in these views since as the branch lengths for the star molecules are increased, the gM increases according to case B of our model such that enhancement is predicted; this is illustrated in Figure 10.

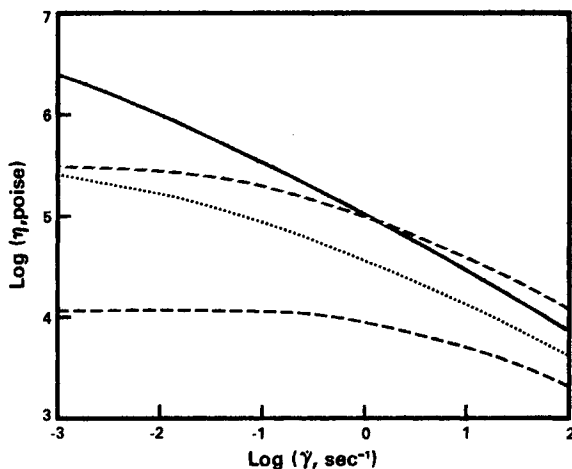


Fig. 10. Predicted effects of LCB at higher levels on flow curve for polyethylene; ---, 1.8 LCB/1000C;, 0.75 LCB/1000C; —, 0.1 LCB/1000C; -.-, linear.

Summary of Effects of Levels of LCB on Rheological Behavior

The description of the flow curve from molecular structure for branching levels ranging from the near linear to highly branched LDPE has been demonstrated. The predicted effects of branching on the flow curve is summarized in Figures 10 and 11. The effects of branching is shown in Figures 10 and 11 to be such that the viscosity at low shear rates can be either substantially elevated or depressed relative to the linear case, depending on the branching level. The reason for this apparently contradictory behavior can be understood as follows. At the lowest branching levels, in which not every molecule contains a branch and the composite sample must be regarded as a blend of linear and more viscous branched species, the viscosity, as depicted in Figure 11, at low shear rates increases with branch level according to eq. (6). In effect, the low shear viscosity increases with branching level because of increasing amounts of the more viscous branched components with increased branching level. As the branching level increases further, the probable fraction of branched species in the sample approaches unity and a maximum is reached in the low shear viscosity, because of the decrease in radius of gyration with increased branching level. The low shear viscosity continues to decrease with branching level because of a corresponding decrease in the radius of gyration with branch level, until the low shear viscosity of the branched material becomes less than the linear material of equivalent molecular weight. This case is depicted in Figure 10. The predicted effects of branching on the low shear viscosity are summarized in the highly schematic representation in Figure 12. The range of branching covered in the figure is from linear HDPE to highly branched LDPE.

Discussion of Approximations

A unique relationship between η_o and $(g\bar{M})_w$ has been demonstrated for the LDPE samples studied here. The uniqueness of a relationship of this sort must be questioned in view of the disturbing results reported in ref. 2. Similar concerns have been reported by Ram and Pederson,⁹ although a seemingly unique relationship was reported by these authors. It is possible that the lack of

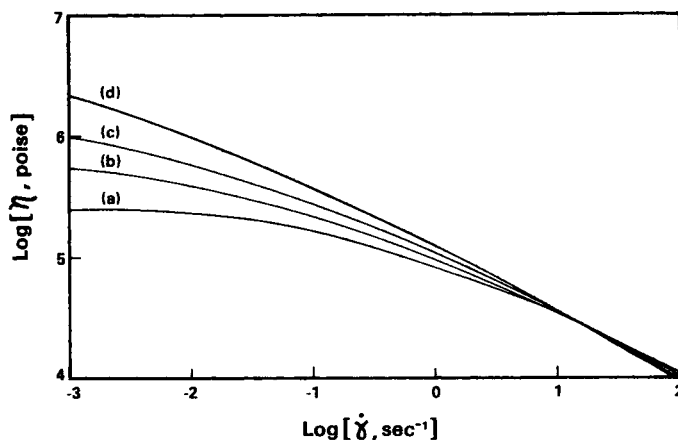


Fig. 11. Predicted effects of LCB at low levels on flow curve of HDPE; (a) linear; (b) 0.025 LCB/1000C; (c) 0.05 LCB/1000C; (d) 0.1 LCB/1000C.

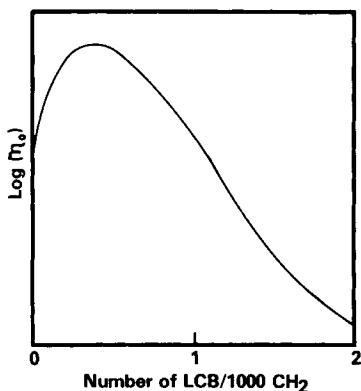


Fig. 12. Schematic representation of predicted effects of branching on Newtonian viscosity (η_o) for samples having identical molecular weight distributions.

uniqueness of the zero shear rate relation reported by Wild, Ranganath, and Knobloch² reflects variations in the linear fraction (molecular weight below ~ 6000) of the LDPE samples examined. In any case, the authors of this article feel that in view of the rather large corrections to the molecular weight distribution (in order to obtain the distribution of gM) and the sensitivity of these calculations to the procedure to obtain the distribution of gM , the uniqueness of the $\eta_o - (gM)_w$ relationship is moot at this time.

The use of the random branching assumption to obtain w_L and w_B is obviously an approximation, which at the present time we are not prepared to deal with in a wholly satisfactory manner. However, this may not be as serious since we have not assumed that branching is independent of molecular weight, but only that it is randomly distributed at a given hydrodynamic volume by GPC.

The use of eq. (2) in Appendix A cannot be rigorously defended, but rather reflects our ignorance as to partitioning of the linear species.

We are presently investigating modifications to the present model to reduce the approximations and assumptions made here. The most significant change will involve the simplification of the blends associated with eqs. (5) and (6). In the present model, the branched component in eq. (5) can contain linear species; even highly branched LDPE contains linear species below molecular weights of approximately 6000. Using eqs. (5) and (6) for the LDPEs studied here, the random branching assumptions (similar to those of Appendix A) to generate probable branched and linear component distributions making up the LDPE samples, eqs. (1) and (2), equations similar to eqs. (3) and (4) can be obtained for totally branched polyethylene. This should yield relationships for totally branched polyethylene that are unique. This also simplifies subsequent applications to HDPE since the probability of a given linear species belonging to the linear component (see Appendix A) of the blend will be $\equiv 1$, simplifying the analysis considerably.

CONCLUSIONS

Because of the low level of branching in HDPE, these materials must be considered to contain both linear and branched species. At any shear rate, a logarithmic rule of mixtures for the steady shearing viscosity has been demonstrated

both for laboratory blends of HDPE/LDPE and HDPE containing few branches.

The description of the flow behavior of polyethylene containing any level of branching can be described by the current model. At extremely low levels of branching, the low shear viscosity is shown to increase with branch level because of an increased concentration of the more viscous branched component. However, as the branching is increased still further, the fraction of branched species in the sample approaches unity and, because of a decrease in the mean-square radius of gyration with branching level, the low shear viscosity goes through a maximum and then continues to decrease with branch level. Consequently, the low shear viscosity can be dramatically higher than for a linear sample of equivalent molecular weight for a sample containing few branches, but considerably lower for samples such as low-density polyethylene having a large branching content.

APPENDIX A

Treatment of Branched HDPE as a Blend of Branched and Linear Distributions

If we are to consider samples containing very low levels of branching, and therefore to be described by equations similar to eqs. (5) and (6), then w_L and w_B must be defined. At low levels of branching not every molecule will contain a long chain branch. The problem of treating the case where the hypothetical blend components making up the real sample is complicated by the fact that eqs. (3)–(6) were developed using LDPE, which itself does not contain only branched species (below ~ 6000 in molecular weight only linear species are assumed present by the Ram and Miltz¹¹ technique of branching determination). Therefore, our procedure of generating the branched and linear distributions must reflect this fact. If w_L is the weight fraction of the linear blend component, \bar{h}_i the weight fraction of species i in the real sample, P_i the probability of species i being linear, and P the probability of a linear species i belonging to the hypothetical linear blend component, then

$$w_L = P \sum_{i=1}^l \bar{h}_i + P \sum_{i=l}^{\infty} \bar{h}_i P_i \quad (\text{A-1})$$

where $M_l \equiv 6000$, $P \equiv 1$ for $M \leq 6000$, and $P \cdot P_i$ the probable weight fraction of i belonging to the linear blend component. From the definitions of P and w_L , it is evident that w_L is a lower limit to P (i.e., $P \geq w_L$). An acceptable upper limit to P can be shown to be $[(w_{L0} - 0.15)/0.85]$, where w_{L0} is the weight fraction of linear species in the real sample. The 0.15 in the above expression is the average weight percent of linear species for the LDPE samples used here. The inclusion of this term and the divisor of 0.85 will guarantee that $P = 0$ for LDPE (i.e., $w_L \equiv 0$) and $P = 1$ when $w_{L0} = 1$. Because of our ignorance regarding P , we shall assume that P is represented by the geometric mean of the extremes of P , w_L and w_{L0} , such that

$$P = \sqrt{\frac{w_L (w_{L0} - 0.15)}{0.85}} \quad (\text{A-2})$$

To obtain P_i we shall assume that the branches are randomly distributed for each i . Consider the random branching of 100 molecules with 100 n_i branches, where n_i is the number of branches per molecule i . The probability (P_i) of a given molecule not containing a branch after the distribution of the 100 n_i branches is

$$P_i = (0.99)^{100 n_i} \quad (\text{A-3})$$

From the definition of w_{L0}

$$w_{L0} = \sum_{i=1}^{\infty} \bar{h}_i P_i \quad (\text{A-4})$$

From eqs. (A-1)–(A-3) we get for w_L

$$w_L = w_{L0}^2 \left(\frac{w_{L0} - 0.15}{0.85} \right) \quad (\text{A-5})$$

and

$$P = \frac{w_{L0}(w_{L0} - 0.15)}{0.85} \quad (\text{A-6})$$

The foregoing analysis leads to a synthesis of linear and branched components such that the new normalized weight percent of i in the linear distribution (\bar{h}_{Li}) is

$$\bar{h}_{Li} = \frac{\bar{h}_i \cdot P_i}{w_{L0}} \quad (\text{A-7})$$

and for the branched component

$$\bar{h}_{Bi} = \frac{\bar{h}_i [1 - PP_i]}{[1 - w_{L0}P]} \quad (\text{A-8})$$

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