

Appraisal of a Molecular Weight Distribution-to-Rheology Conversion Scheme for Linear Polyethylenes

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SYNOPSIS

A theoretical scheme relating quantitatively the rheology of linear polymer melts to molecular weight distribution (MWD) would be of great significance in that it can help interpret polymer rheology and processing behavior in terms of molecular weight characteristics. The present paper is concerned with the appraisal of such a theory—the partition model of Bersted. The theory involves four parameters that are fitted to experimental data on a variety of linear polyethylenes. Although the model does fit the data with better than 10% accuracy, the parameters show some variability that points to theory limitations. An error analysis also shows that this variability is partly accounted for by experimental errors in MWD determination that are amplified in the predicted rheological properties. The rheological properties are shown to be heavily influenced by the high molecular weight tail of the MWD. Errors in MWD determination are detrimental for a MWD-to-rheology conversion, even if a conversion scheme were perfectly accurate. Low levels of long-chain branching that may possibly be present are also detrimental to an MWD-to-rheology conversion. The inverse problem of determining the complete MWD from rheology appears to be practically infeasible for broad MWD polymers. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The rheology of polymer melts depends strongly on the underlying molecular structure: molecular weight and molecular weight distribution (MWD) and long-chain branching (the latter only for branched polymers). A twofold increase in molecular weight results in a 10-fold increase in zero-shear viscosity; a high molecular weight tail enhances elasticity significantly, whereas the shear viscosity at high shear may practically be unaffected. These examples show that different rheological properties exhibit different degrees of sensitivity to the underlying MWD.

It would be of great significance to establish a quantitative interrelation between rheology and molecular weight characteristics. Such a scheme would allow prediction of rheological properties from

MWD (and possibly vice versa) and also help interpret processing behavior in terms of molecular weight characteristics, therefore providing guidance for modification (e.g., tailor-made MWD, blending, etc.). Of particular interest would be a conversion scheme that would predict MWD from rheological properties, as it would allow the use of on-line rheometry for polymer reactor control.

There has been a considerable amount of work reported on relating the rheology of molten polymers to molecular weight and MWD. Recent reviews on the subject have been offered by Pearson,¹ Briedis,² and Tuminello.³ Several theoretical conversion schemes have been proposed with varying degrees of sophistication. However, testing of these theories is often performed on idealized systems, e.g., monodisperse polymers and their binary blends. The objective of the present paper is to evaluate Bersted's⁴⁻¹¹ conversion scheme on broad, polydisperse polymers of wide-ranging MWD that are typically encountered in industrial practice. The evaluation is based on linear viscoelastic data, a more stringent test than

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the use of steady-shear viscosity data that is commonly employed. The list of polymers included for testing vary both in molecular weight and MWD and therefore provides a critical test of the conversion scheme that has not been attempted in the past.

THEORETICAL: THE PARTITION MODEL

The MWD-to-rheology conversion scheme selected for appraisal is the partition model of Bersted,⁴⁻¹¹ which has also been recently employed by Tuminello and Cudre-Mauraux.¹² The model is best described in terms of four major assumptions about the effect of shear rate on the spectrum of relaxation times:

- (i) The spectrum of relaxation times is cut off at a maximum-allowed relaxation time τ_c .
- (ii) It is assumed that the cut-off relaxation time is inversely proportional to the shear rate, i.e., $\tau_c \propto 1/\dot{\gamma}$.
- (iii) In addition to the longest relaxation time for a given molecule, the molecular chain undergoes relaxations characteristic of all molecular weights less than its own molecular weight.
- (iv) The relaxation times associated with a given molecular species are independent of communal properties in a polydisperse mixture.

These assumptions imply that at any shear rate, or, more generally, at any characteristic time scale of deformation τ_c , there corresponds a critical molecular weight M_c . The MWD and the relaxation spectrum are partitioned (by M_c and τ_c , respectively) into two classes; the relaxation times are partitioned into operative (smaller than τ_c) and inoperative (larger than τ_c), i.e., the relaxation spectrum is cut off at τ_c . The molecular weights are partitioned into fully relaxed (smaller than M_c) and partially relaxed (larger than M_c). Those molecular weights larger than M_c behave rheologically as if they were of molecular weight M_c (since all their longer relaxation times are cut off), i.e., the MWD, as reflected rheologically, is altered dynamically. In other words, the effect of a given rate of deformation is to truncate the linear viscoelastic spectrum at τ_c and alter the MWD for $M > M_c$. Mathematically,

$$H(\tau, \tau_c) = \begin{cases} H(\tau) & \text{for } \tau \leq \tau_c \\ 0 & \text{for } \tau > \tau_c \end{cases} \quad (1)$$

MWD: $w_i(M_i)$

$$= \begin{cases} w_i(M_i) & \text{for } M_i \leq M_c \\ \sum_{M_c}^{\infty} w_j(M_j) & \text{for } M_i > M_c \end{cases} \quad (2)$$

Given the above partitioning, the equations of linear viscoelasticity are applicable but with the effective relaxation spectrum. The viscosity is

$$\eta_0(\tau_c) = \int_0^{\tau_c} H(\tau) d\tau \quad (3)$$

Differentiating eq. (3), we get

$$H(\tau_c) = \frac{d\eta_0(\tau_c)}{d\tau_c} \quad (4)$$

The effective weight-average molecular weight M_w^* is

$$M_w^* = \sum_{i=1}^{c-1} w_i M_i + M_c \sum_{i=c}^{\infty} w_i \quad (5)$$

The zero-shear viscosity is related to the average molecular weight through

$$\eta_0(M_w^*) = k_1 (M_w^*)^{\alpha_1} \quad (6)$$

where $\alpha_1 \approx 3.4$ (Ref. 13).

The cutoff relaxation time is related to molecular weight M_c through a similar relationship:

$$\tau_c = k_2 (M_c)^{\alpha_2} \quad (7)$$

Using eqs. (5)–(7) in eq. (4),

$$H(\tau_c) = \frac{k_1 \alpha_1 (M_w^*)^{(\alpha_1-1)} \left(\sum_{i=c}^{\infty} w_i \right)}{k_2 \alpha_2 M_c^{(\alpha_2-1)}} \quad (8)$$

Equation (8) provides the relaxation spectrum in terms of the four parameters k_1 , α_1 , k_2 , and α_2 .

The procedure to calculate the relaxation spectrum, given the MWD and the model parameters k_1 , α_1 , k_2 , and α_2 is

Step 1 For every molecular weight fraction M_i , calculate the effective average M_w^* from eq. (5) for $M_c = M_i$.

Step 2 Calculate the relaxation time from eq. (7).

Step 3 Calculate the relaxation strength from eq. (8).

Step 4 Repeat Steps 1–3 until the complete relaxation spectrum is computed. Then, calculate the dynamic moduli from

$$G'(\omega) = \int_{-\infty}^{+\infty} H(\tau) \frac{(\omega\tau)^2}{1 + (\omega\tau)^2} d \ln \tau \quad (9.1)$$

$$G''(\omega) = \int_{-\infty}^{+\infty} H(\tau) \frac{(\omega\tau)}{1 + (\omega\tau)^2} d \ln \tau \quad (9.2)$$

EXPERIMENTAL

Three sets of resins were selected for testing. The first set is a series of blends of a low molecular weight high-density polyethylene (LMW-HDPE) and a high molecular weight HDPE (HMW-HDPE). The blends are indicated in Table I according to the nominal percentage of high molecular weight component (%HMW). These blends were prepared by dissolving weighted amounts of the components in xylene, allowing the solvent to evaporate, and then vacuum drying at 60°C for 72 h.

The second set of resins is a series of typical commercial HDPEs (HDPE-1,2,3). The third set is a series of commercial linear low-density polyethylenes (LLDPE-1,2,3,4).

Dynamic rheological data were obtained with the Rheometrics Dynamic Analyzer #2, operating in the

oscillatory shear mode (parallel plates), in the frequency range 0.025–400 s⁻¹. Strain was 20%, which was verified to be in the linear viscoelastic region. The temperature of measurement was 190°C for all HDPEs and 150°C for all LLDPEs.

Molecular weight distribution (MWD) was determined by GPC. The MWDs are shown in Figure 1 for HDPE blends, Figure 2 for HDPE-1,2,3, and Figure 3 for LLDPEs. Molecular weight averages and polydispersity numbers are summarized in Table I.

RESULTS AND DISCUSSION

Computational Considerations

The test of the theory is how well it fits experimental data. The model constants (k_1 , α_1 , k_2 , α_2) must therefore be fitted to rheological data and an appraisal be made of the fitting power of the theory and of the variability of the constants. Note that according to the theory the four constants are independent of molecular weight and MWD.

The constants k_1 and α_1 could be determined independently from zero-shear viscosity data. However, zero-shear viscosities are difficult to obtain unambiguously for commercial polydisperse melts, especially for polyethylenes. The reason is that the terminal region (the low shear rate region where viscosity approaches its zero-shear value) is at very low shear rates (or frequencies, for dynamic data)

Table I Identification and Characteristics of Resins Studied

Resin	Melt Index (g/10 min)	Density (g/cm ³)	M_w	M_w/M_n	M_z/M_w
LMW-HDPE	33	0.96+	57,640	7.34	8.76
5% HMW	—	—	63,740	8.43	8.59
10% HMW	—	—	90,000	11.13	10.63
20% HMW	—	—	165,500	15.98	9.03
40% HMW	—	—	247,100	14.07	7.80
70% HMW	—	—	321,900	11.81	4.43
HMW-HDPE	0.6 HLMI	0.935	414,400	5.02	3.53
HDPE-1	0.2	0.960	230,500	11.85	7.76
HDPE-2	0.9	0.960	166,400	15.48	11.02
HDPE-3	6.0	0.960	92,720	11.10	11.07
LLDPE-1	1.0	0.918	119,300	3.95	3.81
LLDPE-2	2.0	0.918	102,800	3.79	4.03
LLDPE-3	5.3	0.934	72,430	3.34	3.55
LLDPE-4	13.0	0.926	51,840	3.44	3.19

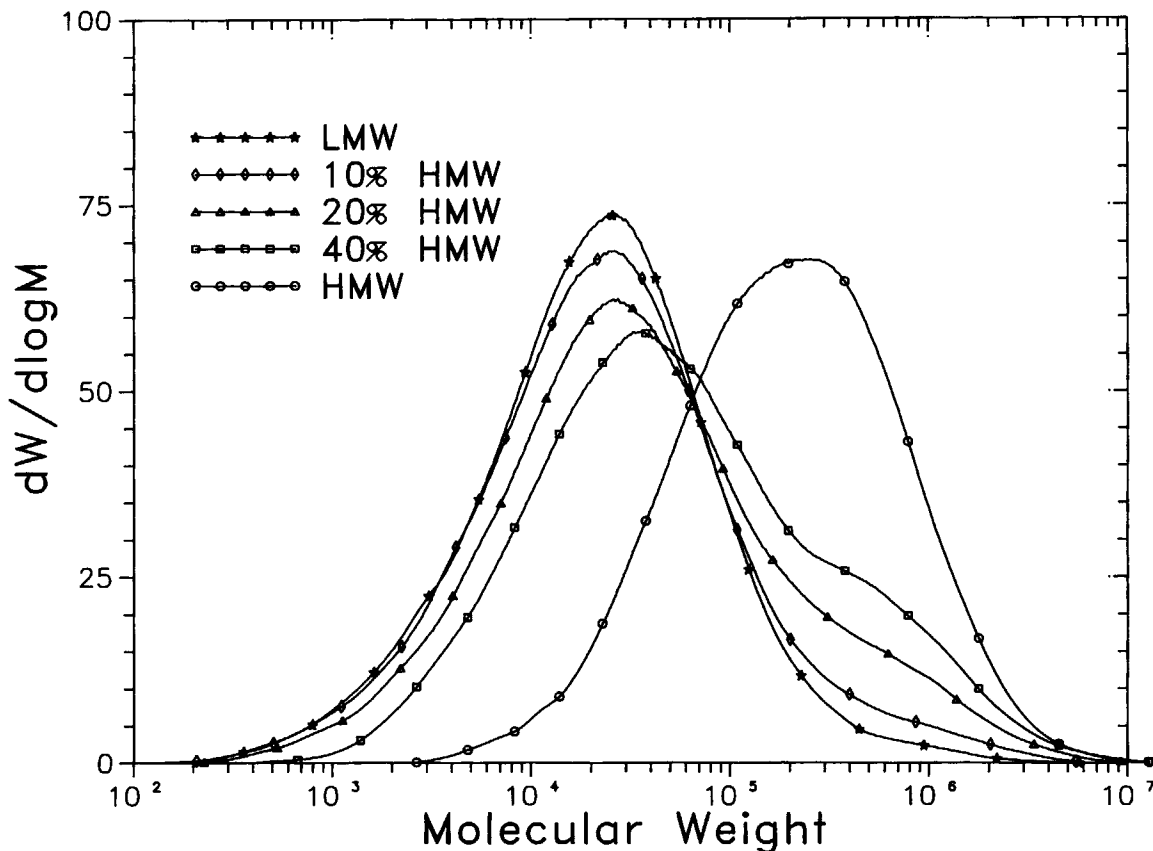


Figure 1 MWD of HDPE blends.

that are inaccessible with current rheological instruments. The usual determination-by-extrapolation of higher shear rate data may introduce errors detrimental to a theory that aspires to accuracy of a few percent. The high sensitivity ($\alpha_1 \approx 3.4$) of viscosity to molecular weight also precludes the use of literature correlations, given the variability of molecular weights determined by GPC at different laboratories.

The procedure finally adopted in this work was to fix the value of α_1 at 3.4 ($\alpha_1 = 3.4$). The 3.4-power dependence of viscosity on molecular weight has been observed repeatedly in the literature¹⁴ (the applicability of the 3.4-power dependence for the data of the present work is demonstrated in Figure 4. Note that these zero-shear viscosities were obtained by extrapolating the complex viscosity data, using the Sabia equation¹⁵). The remaining three constants, k_1 , k_2 , and α_2 , were determined by least-squares fit to dynamic data as follows: For a given case (e.g., HDPE blends), the constants k_1 , k_2 , and α_2 were determined by the requirement that they minimize.

$$\sum_{i=1}^N \left[\log^2 \left(\frac{G'_{i,\text{calc}}}{G'_{i,\text{exp}}} \right) + \log^2 \left(\frac{G''_{i,\text{calc}}}{G''_{i,\text{exp}}} \right) \right]$$

where N is the number of dynamic data points. The subscripts "calc" and "exp" indicate "calculated" and "experimental" values, respectively.

The fitting of the parameters was performed for the highest molecular weight of the series (HMW-HDPE for HDPE, LLDPE-1 for LLDPE). The α_2 value was then fixed and *only the constants* k_1 and k_2 were fitted parameters for the remaining polymers. Note that k_1 and k_2 enter linearly in the equations [eq. (8)], i.e., they correspond to coordinate shifts in a log-log plot (of modulus vs. frequency data). The shape of the predicted rheological functions depends only on α_1 and α_2 .

Model Fitting

Case I: HDPE Blends

The case of the HDPE blends was selected as a particularly severe test of the theory since the blend

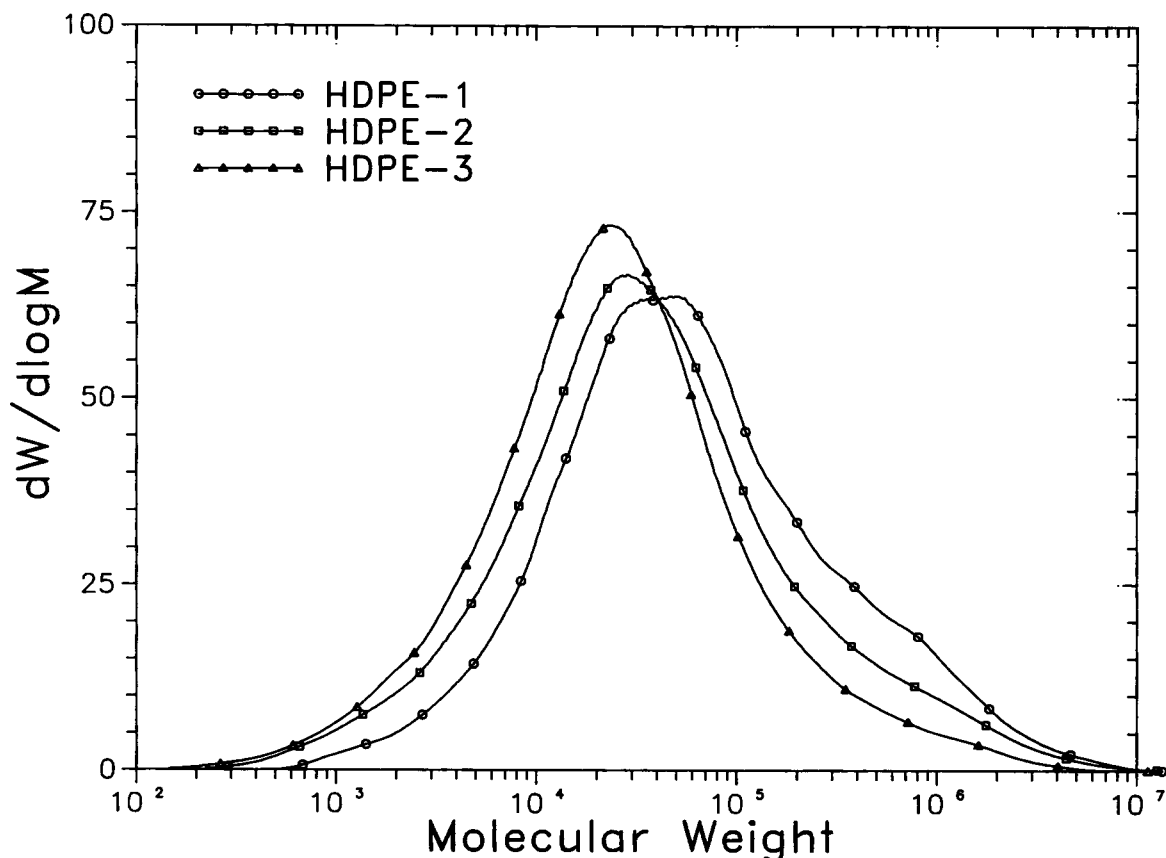


Figure 2 MWD of HDPEs.

components have very different molecular weights. As discussed earlier, the parameters k_1 , k_2 , and α_2 were fitted for HMW-HDPE (the highest molecular weight). The fitted value of α_2 was 2.905, which was then held fixed when fitting k_1 and k_2 for the remaining members of the set. The fitted values are listed in Table II.

Comparison of theory predictions and experimental data is shown in Figure 5(a) for storage modulus, Figure 5(b) for loss modulus, and Figure 5(c) for complex viscosity. It can be seen that the agreement is best for the highest molecular weight (HMW-HDPE) and reasonably good for the blends, but marginal, by comparison, for the pure low molecular weight (LMW-HDPE). This points to an inadequacy of the theory in regard to the relaxation time-molecular weight relationship [eq. (7)]. A dependence of k_2 on molecular weight could be accommodated in the way that the theory was implemented in this work. However, the discrepancy shown in Figure 5(a)-(c) (i.e., $\alpha_2 = 2.905$ fits well all blends having a component of HMW but not well the low molecular weight component) indicates a depen-

dence of α_2 on molecular weight distribution. Further discussion on this will be given later.

Case II: HDPE

The α_2 parameter calculated previously ($\alpha_2 = 2.905$) was held fixed and only k_1 and k_2 were free to fit for a series of commercial high-density polyethylenes. Fitted parameters are summarized in Table II, whereas comparison of prediction with experimental data is shown in Figure 6(a)-(c) for storage modulus, loss modulus, and complex viscosity, respectively. The agreement is good considering that in this case only coordinate shifts were involved (k_1 and k_2 parameters), whereas the shape of the rheological functions was predicted *a priori*.

Case III: LLDPE

The last test of the theory was on a series of LLDPEs with relatively narrower molecular weight distribution. The k_1 , k_2 , and α_2 parameters were fitted for LLDPE-1, giving a value of 2.575 for α_2 . The α_2 parameter was then fixed and k_1 and k_2 were deter-

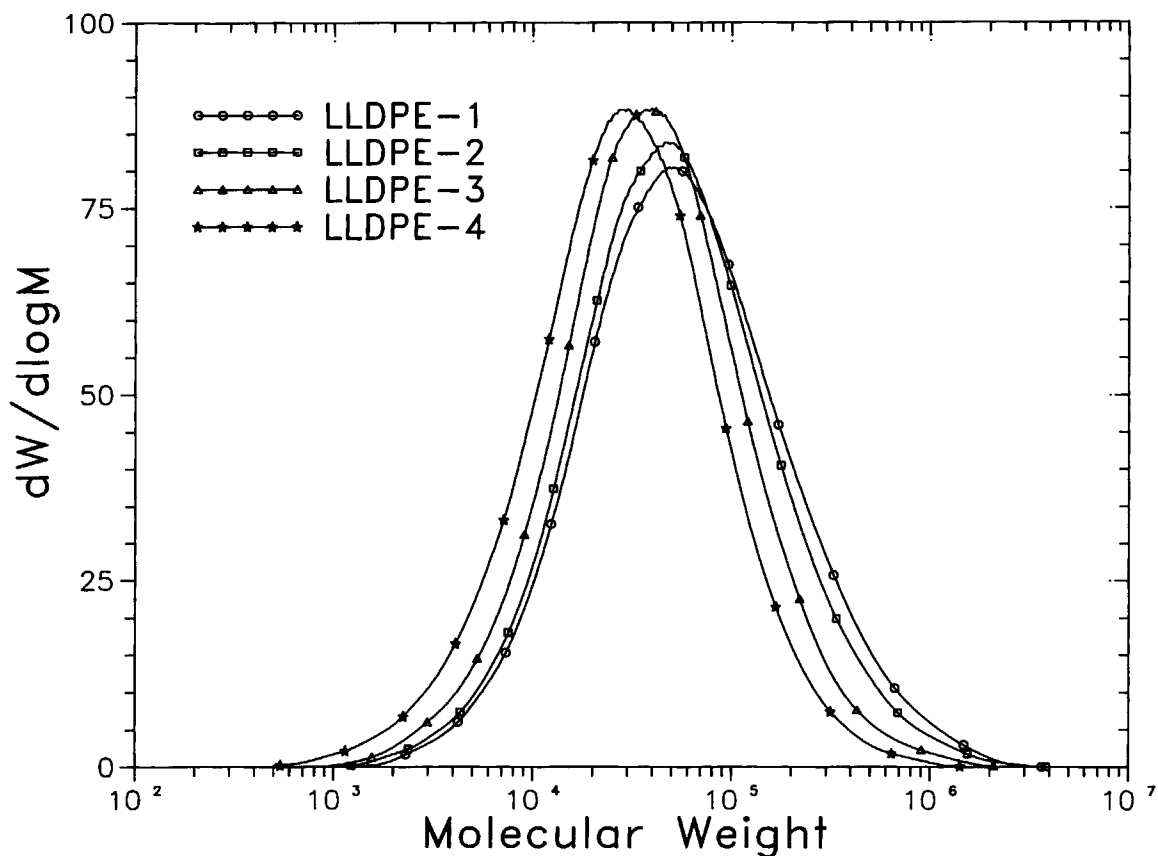


Figure 3 MWD of LLDPEs.

mined for the remaining members of the series. The fitted parameters are summarized in Table II. Comparison of prediction with experiment is shown in Figure 7 (a)–(c) for storage modulus, loss modulus, and complex viscosity, respectively. The agreement is good, and as in previous cases, it is always better than 10%.

Model Appraisal

As discussed earlier, the test of the theory consists in answering the following two questions:

- (i) How well the four-parameter partition model (k_1 , α_1 , k_2 , α_2) fits *individually* rheological data (e.g., for a given polymer melt).
- (ii) Whether the parameters are material constants or vary widely.

The first question has already been answered positively: The theory does fit the data with better than 10% accuracy. The second question, however, points to the deficiencies of the model. As developed orig-

inally,^{4,5} the four parameters are material constants, independent of molecular weight and distribution. Examination of Table II, however, shows that the parameters do vary. The fact that a single value of the α_2 parameter fits a wide range of resins is welcome, but a different value of α_2 was needed for narrow distributions ($\alpha_2 = 2.575$ for LLDPEs) as opposed to $\alpha_2 = 2.905$ for broad HDPEs. In addition, there is still the variability of k_1 and k_2 (shift factors) to be accounted for.

The variability of k_1 is associated with the applicability of the zero shear viscosity–weight average molecular weight relationship [eq. (6)]:

$$\eta_0(M_w) = k_1 M_w^{\alpha_1} \quad (10)$$

This relationship has been established for narrow fractions and its validity for polydisperse systems may be questionable. Unfortunately, the variation of k_1 shown in Table II does not seem to correlate with molecular weight or MWD in a simple way. Moreover, it is nearly constant for certain combinations (HDPE-1 and 2, LLDPE-1 and 2), which

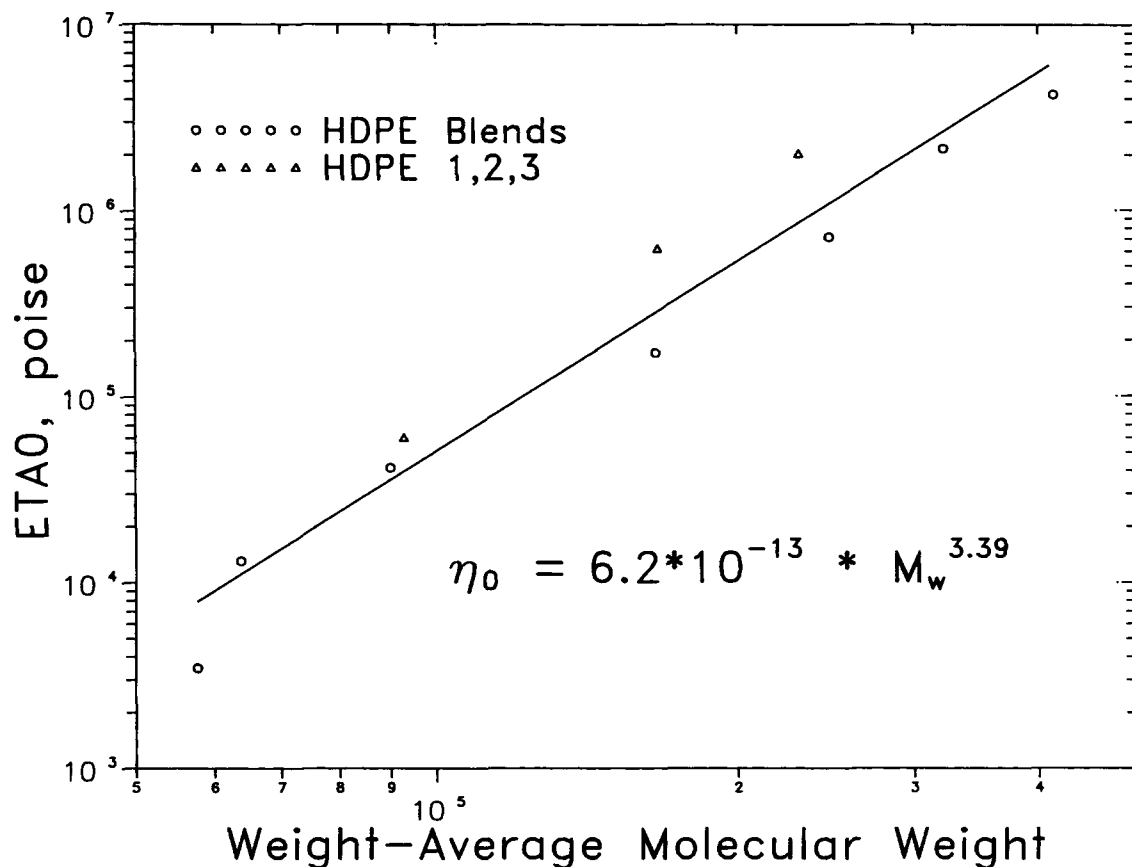


Figure 4 Extrapolated zero-shear viscosity vs. weight-average molecular weight for the resins used in this work.

suggests that the k_1 variation may be confounded by experimental error in MWD determination. An example can reinforce this point: Taking $\alpha_1 = 3.4$ and assuming an error in M_w of $\pm 10\%$ results in an

Table II Partition Model Parameters ($\alpha_1 = 3.4$)

Resin	$\log_{10} k_1$	$\log_{10} k_2$	α_2
LMW-HDPE	-12.64	-18.30	2.905 (fixed)
5% HMW	-12.31	-17.15	2.905 (fixed)
10% HMW	-12.40	-17.23	2.905 (fixed)
20% HMW	-12.66	-17.28	2.905 (fixed)
40% HMW	-12.50	-16.99	2.905 (fixed)
70% HMW	-12.34	-16.53	2.905 (fixed)
HMW-HDPE	-12.40	-16.50	2.905 (free)
HDPE-1	-12.17	-16.41	2.905 (fixed)
HDPE-2	-12.16	-16.65	2.905 (fixed)
HDPE-3	-12.23	-16.86	2.905 (fixed)
LLDPE-1	-12.00	-14.77	2.575 (free)
LLDPE-2	-12.00	-14.88	2.575 (fixed)
LLDPE-3	-11.96	-14.92	2.575 (fixed)
LLDPE-4	-11.85	-14.72	2.575 (fixed)

error of $\pm 40\%$ in zero shear viscosity, i.e., any error in molecular weight is amplified to the 3.4-power in the predicted viscosity.

The variation of k_2 is larger and more disturbing: The theory assumes that the relaxation times of a given molecular chain are independent of communal properties, i.e., unaffected by polydispersity. However, it is known¹⁶ that blending of narrow fractions alters the relaxation times of the components, as compared to relaxation times in the pure state; the relaxation times of the shorter molecules become larger while those of the longer molecules become shorter, a result that is in accord with reptation theory.¹⁷ The experimental fact of the shift in relaxation times of narrow fractions upon blending is sometimes expressed as

$$\tau_{i,m} = \tau_i \left(\frac{M_w}{M_i} \right)^\gamma \quad (11)$$

where τ_i is the relaxation time of pure fraction M_i ; $\tau_{i,m}$, the relaxation time of i -th component in mix-

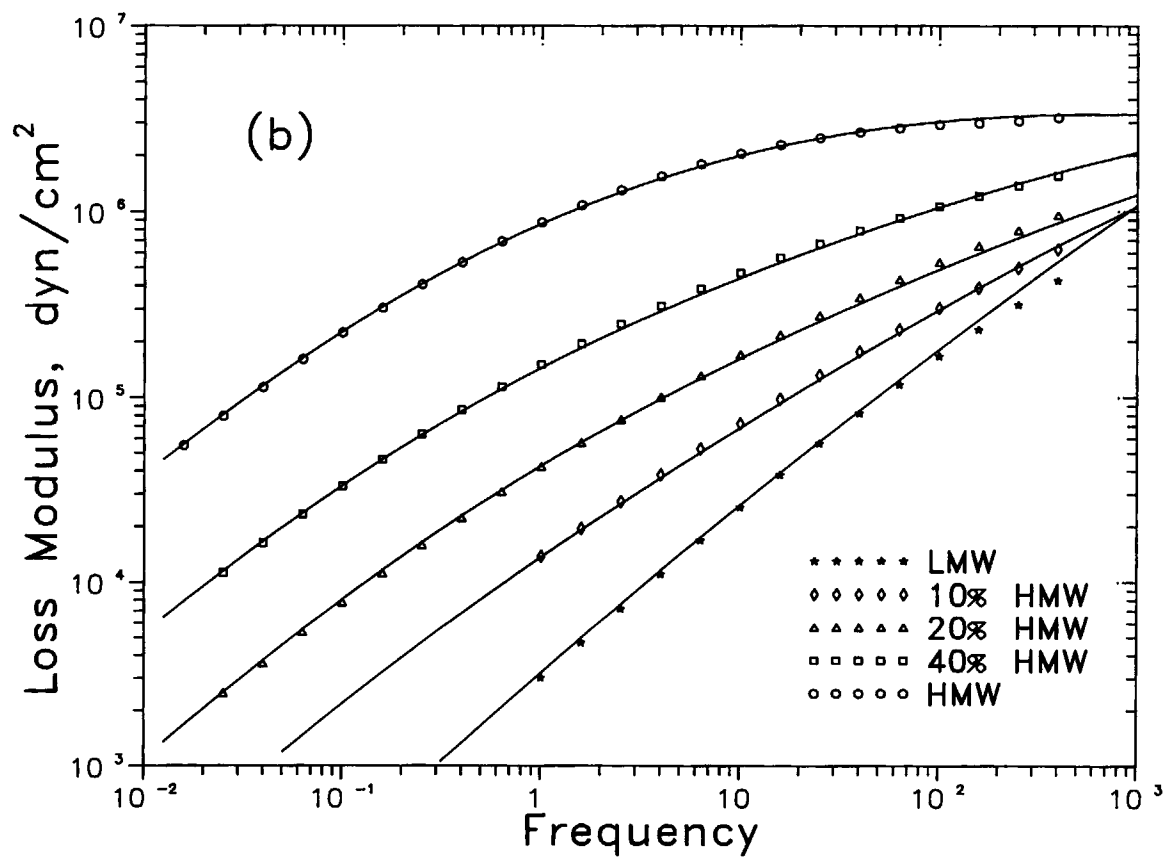
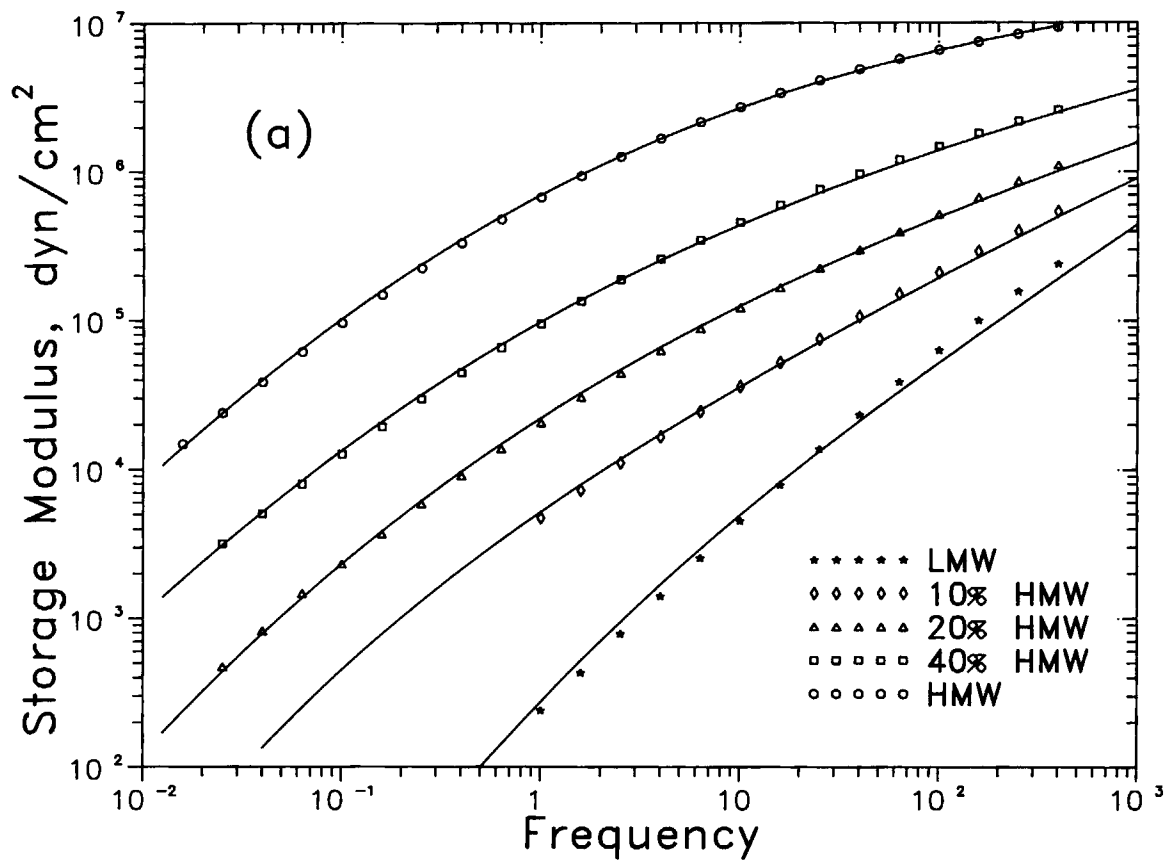


Figure 5 Comparison of experimental data (symbols) with partition model predictions (lines) for HDPE blends: (a) storage modulus; (b) loss modulus; (c) complex viscosity.

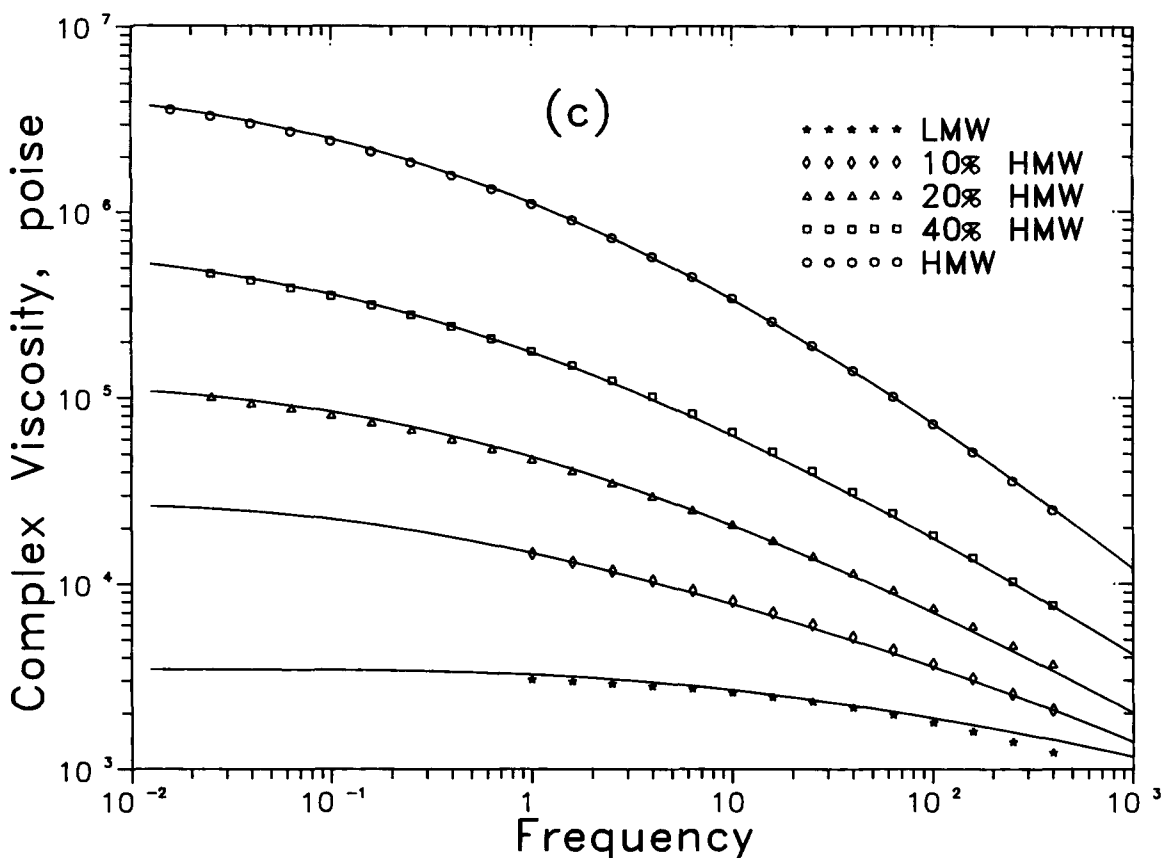


Figure 5 (Continued from the previous page)

ture; and M_w , the weight-average molecular weight of mixture.

Other shifts have also been proposed,¹⁸ which are essentially generalizations of eq. (11). Assuming the validity of eq. (11), then eq. (7) should have been restated as

$$\tau_c = k'_2 M_c^{\alpha'_2} \left(\frac{M_w}{M_c} \right)^\gamma = (k'_2 M_w^\gamma) M_c^{\alpha'_2 - \gamma} \quad (12)$$

i.e.,

$$k_2 = k'_2 M_w^\gamma \quad \text{and} \quad \alpha_2 = \alpha'_2 - \gamma \quad (13)$$

Equation (13) shows that the parameter k_2 actually depends on molecular weight. A plot of k_2 vs. M_w in Figure 8, for the HDPEs, shows a definite trend and the slope of $\gamma = 1.1$ is in accord with similar reported values.¹⁸

Therefore, an improvement of the theory along the lines suggested by eq. (11) is possible. However, it is still difficult to make unambiguous judgments on this matter, since errors in the molecular weights

contribute heavily [$\alpha_2 = 2.9$ in eq. (7), and, therefore, any error in molecular weight M_c is amplified in the calculated relaxation time τ_c], as in the case of the viscosity-molecular weight relationship.

Errors in the experimental rheological data could also have contributed to the observed variability in the k_1 and k_2 parameters but not significantly. The reproducibility of the rheological data was better than 5%, as quantified by the relative standard deviation on replicate measurements. By contrast, the relative standard deviation of average molecular weights determined by GPC was in the 5–15% range. This 5–15% error in molecular weight becomes 18–60% when raised to the 3.4-power (for the conversion to viscosity), i.e., it is amplified. Note that if a rheology-to-MWD conversion were possible, then the comparatively smaller rheological errors would be further attenuated with the conversion. For example, a 5% error in viscosity would correspond to $(1.05^{1/3.4} - 1) \times 100 = 1.5\%$ error in molecular weight. The problem of rheology-to-MWD conversion is addressed in the Appendix.

To illustrate that errors in molecular weight and MWD, as determined by GPC, may be detrimental

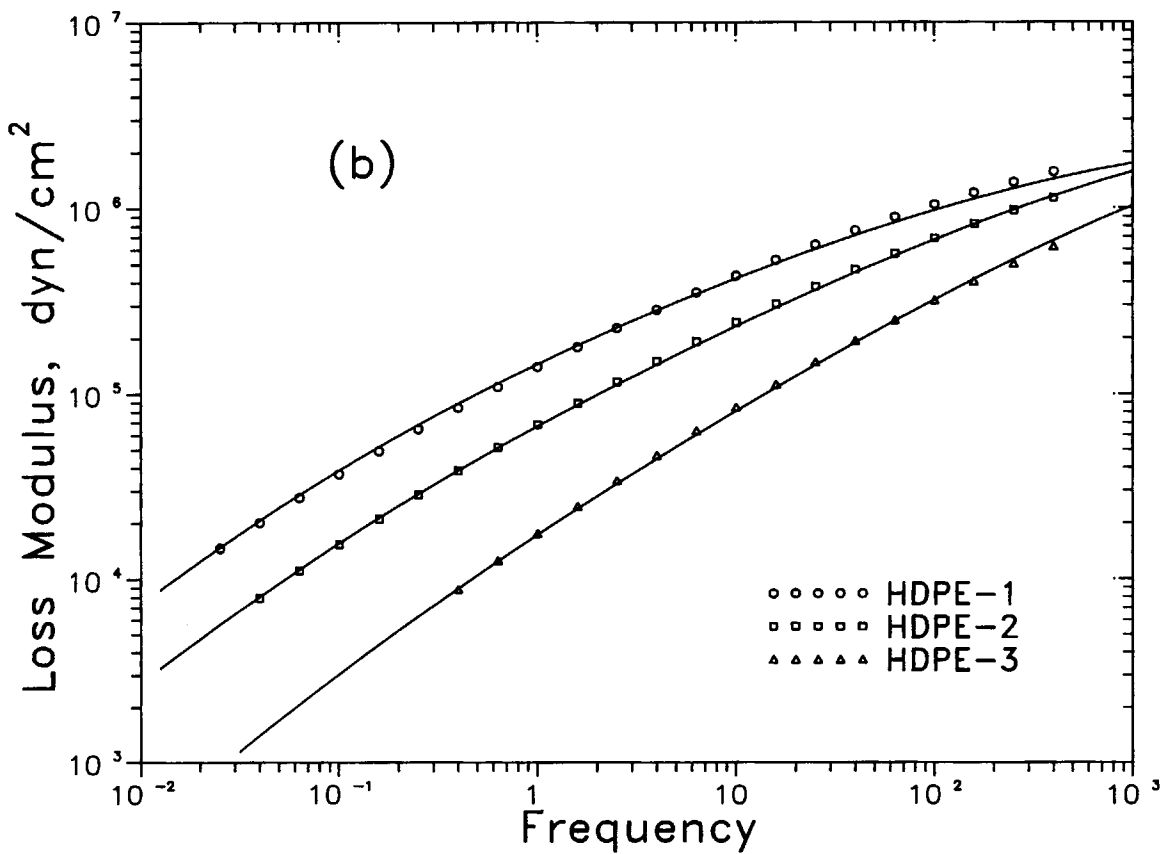
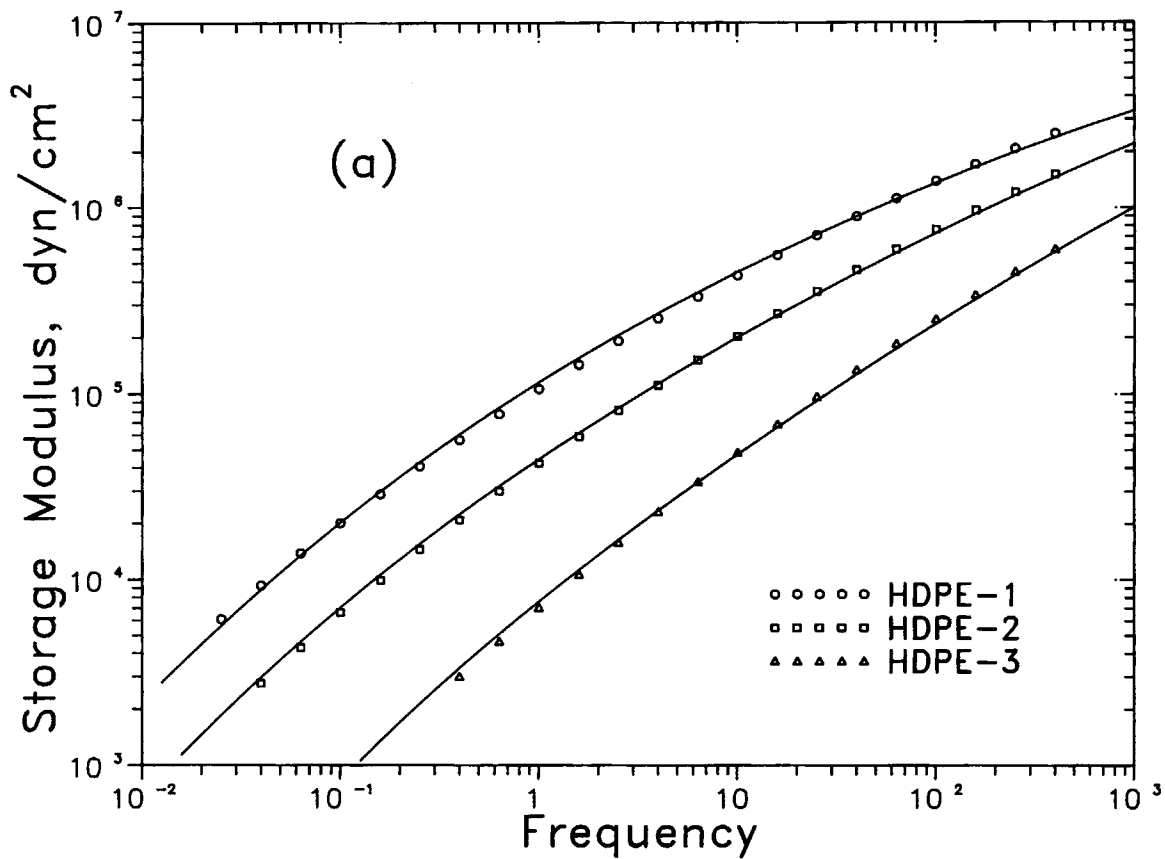


Figure 6 Comparison of experimental data (symbols) with partition model predictions (lines) for HDPEs: (a) storage modulus; (b) loss modulus; (c) complex viscosity.

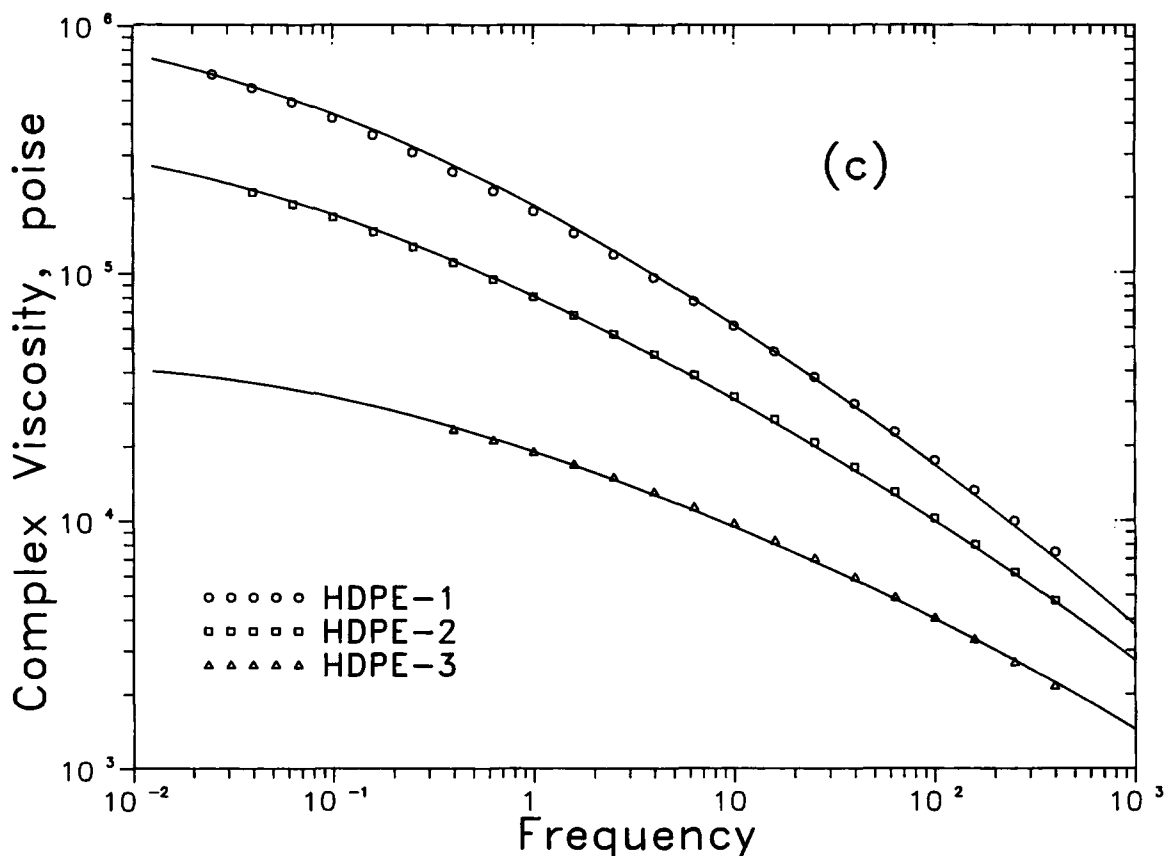


Figure 6 (Continued from the previous page)

for an MWD-to-rheology conversion scheme, a simple computational experiment was performed. The MWD data of HMW-HDPE was modified by excluding a portion of the high molecular weight (MW) tail beyond a certain molecular weight. In the first case, the top 0.5% (by weight) of the high MW tail was excluded (for HMW-HDPE, the top 0.5% is over $MW = 4.3 \times 10^6$, as determined from the original GPC). In the second case, the top 1.0% of the high MW tail was excluded (over $MW = 3.2 \times 10^6$).

These modifications on the MWD were thought to be within the reproducibility of GPC, i.e., similar to the expected errors in GPC. The idea behind the computational experiment was to see how GPC errors propagate in the predicted rheological properties.

The rheological properties were determined for the original MWD and the two modified cases using the partition model parameters of the original MWD. Results are plotted in Figure 9. Obviously, the predicted rheological response (G') is dramatically different for the three cases. Comparative data

are listed in Table III. Note that while the M_w changes by a factor of 1.10 (10%) and the M_z/M_w changes by a factor of 1.34, the predicted viscosity changes by a factor of 1.43 ($=1.10^{3.4}$) and the compliance (J_e^0) changes by a factor of 5.92, i.e., an error in MWD is amplified strongly in the predicted rheological response, particularly in the elastic properties.

The above example illustrates that the extreme sensitivity of rheology to MW and MWD places extraordinary requirements of accuracy on the method for determining MWD, if a MWD-to-rheology conversion scheme is to succeed. It is unlikely that these requirements can be satisfied by the present MWD determination techniques on a routine basis for commercial linear polyethylenes. It must also be noted that extra caution needs to be exercised when evaluating MWD-to-rheology conversion schemes so that potential errors in MWD are not confounded with model inadequacies of the conversion scheme.

Finally, a factor that can undermine the MWD-to-rheology conversion is the possibility of minute amounts of long-chain branching (LCB) that may

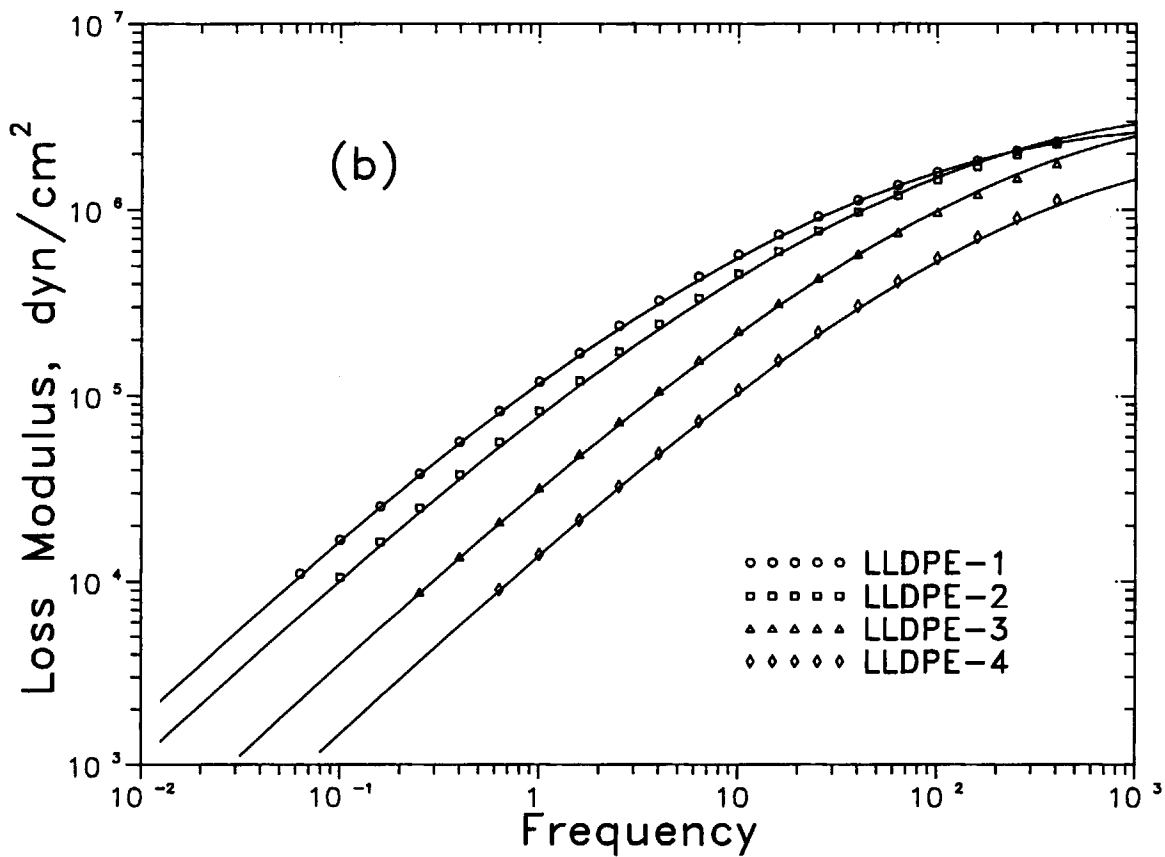
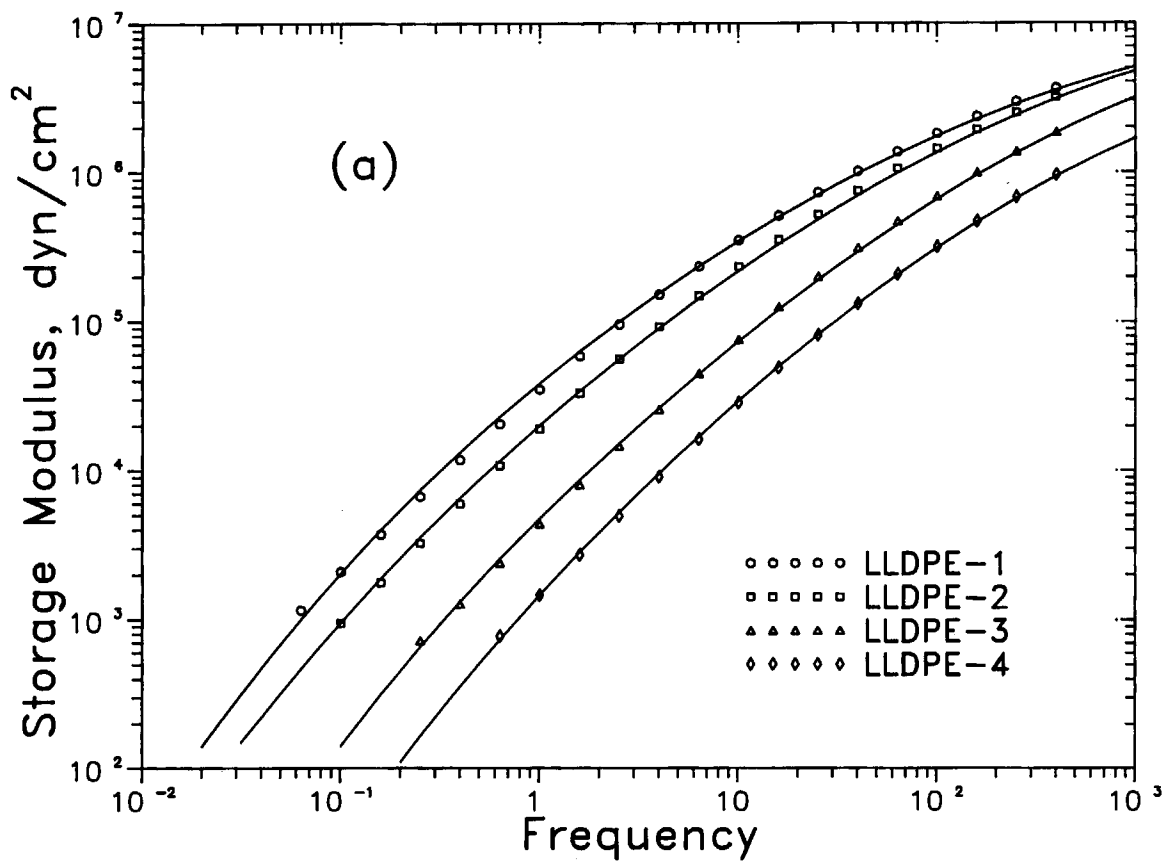


Figure 7 Comparison of experimental data (symbols) with partition model predictions (lines) for LLDPEs: (a) storage modulus; (b) loss modulus; (c) complex viscosity.

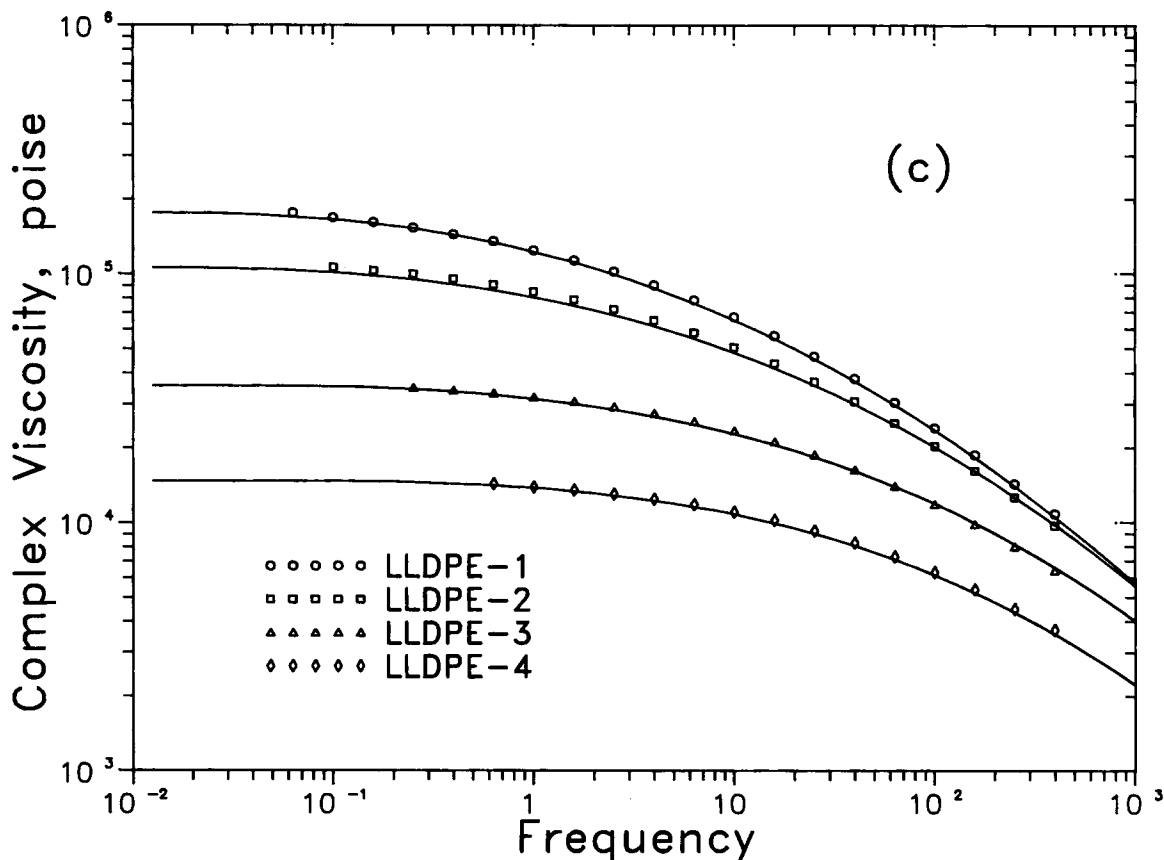


Figure 7 (Continued from the previous page)

be present, even for “linear” polyethylene (e.g., LCB may be introduced during the pelletization of the reactor powder). Figure 10 shows GPC and rheology data on HDPE samples that have been put through an extruder. Whereas the MWDs (as determined by GPC) are shown to superimpose within experimental error [Fig. 10(a)], the rheological properties show a significant and systematic change, consistent with the expected generation of LCB. Similarly, addition of peroxide alters dramatically the rheological response [Fig. 11(b)], whereas the MWDs are nearly unchanged [Fig. 11(a)]. If an MWD-to-rheology conversion scheme was employed in the above cases, an erroneous rheology prediction would result (even if the MWD-to-rheology conversion scheme were perfectly accurate for a linear polymer).

Discrimination among Different Molecular Weight Contributions to Rheological Response

A very important aspect of the partition model is that it can provide a quantitative measure of how

different molecular weights contribute to the various rheological properties at various frequencies. The point will be illustrated with an example: a typical high-density polyethylene resin (HMW-HDPE, Table I) with an MWD extending over four decades of molecular weights.

As can be observed from the defining equations, the storage and loss modulus at a given frequency are sums of contributions from all molecular weights, i.e.,

$$\begin{aligned} G'(\omega) &= \int_{-\infty}^{+\infty} H(\tau) \frac{(\omega\tau)^2}{1 + (\omega\tau)^2} d \ln \tau \\ &= \int_{-\infty}^{+\infty} H(\tau) \frac{(\omega\tau)^2}{1 + (\omega\tau)^2} \frac{d \ln \tau}{d \ln M} d \ln M \end{aligned}$$

or

$$G'(\omega) = \sum_{i=1}^{\infty} g'_i(\omega) \Delta \log M_i \quad (14)$$

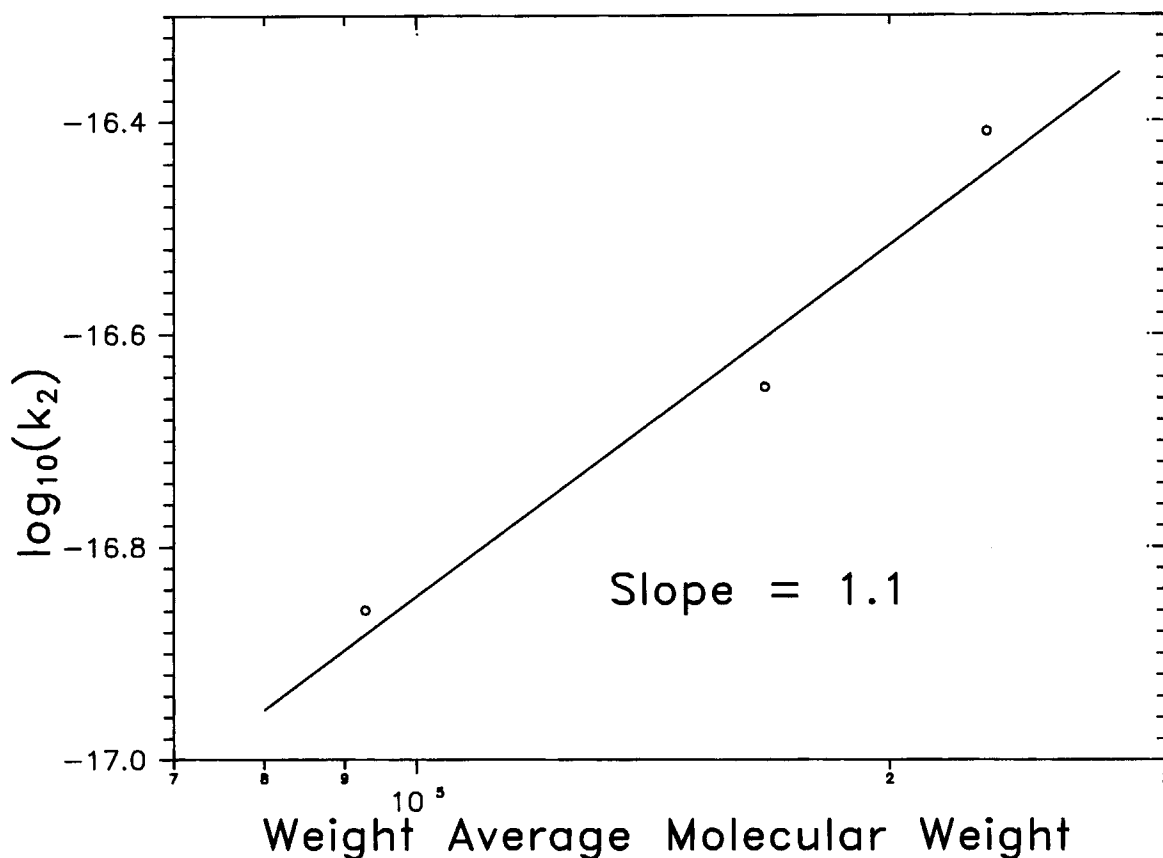


Figure 8 Dependence of k_2 parameter on M_w for HDPEs.

$$g'_i(\omega) = H(\tau_i) \frac{(\omega\tau_i)^2}{1 + (\omega\tau_i)^2} \frac{d \ln \tau}{d \ln M} \ln(10) \quad (15)$$

where $g'_i(\omega)$ is the contribution to $G'(\omega)$ from M_i . Similarly,

$$G''(\omega) = \sum_{i=1}^{\infty} g''_i(\omega) \Delta \log M_i \quad (16)$$

Normalized contributions are defined as

$$g'_{n,i}(\omega) = 100 \frac{g'_i(\omega)}{G'(\omega)} \quad (17)$$

$$g''_{n,i}(\omega) = 100 \frac{g''_i(\omega)}{G''(\omega)} \quad (18)$$

so that the area under the $g'_{n,i}$ vs $\log M$ and $g''_{n,i}$ vs. $\log M$ curves is 100 (same normalization as for the MWD, so that they can be superimposed).

The usefulness of such a plot is that the percentage of $G'(\omega)$ contributed by molecular weights

in the range $(M_i, M_i + d \log M_i)$ is simply $g'_{n,i} \times d \log M_i$. Therefore, the normalized contribution curves $g'_{n,i}$ vs $\log M_i$ and $g''_{n,i}$ vs $\log M_i$ are distributions similar to the MWD and can be plotted over the same axes. *The location and breadth of the distribution curves characterize the contribution of molecular weights to the rheological function under consideration.*

A normalized contribution plot is given in Figure 12(a) for the storage modulus at three frequencies. The MWD is also plotted for reference purposes. It can be readily seen that the storage modulus at the lowest frequency (10^{-2} s^{-1}) is made up of contributions from molecular weights in the range 10^6 – 10^7 . In contrast, at the highest frequency (10^{-2} s^{-1}), the distribution curve is broader (observe the lower peak) and shifted to more than one decade lower. This plot quantifies the empirical observation that the high end of the MWD controls the elastic response at low frequencies. It is apparent from Figure 12(a) that the greatest sensitivity to high molecular weight contributions is displayed at the lowest fre-

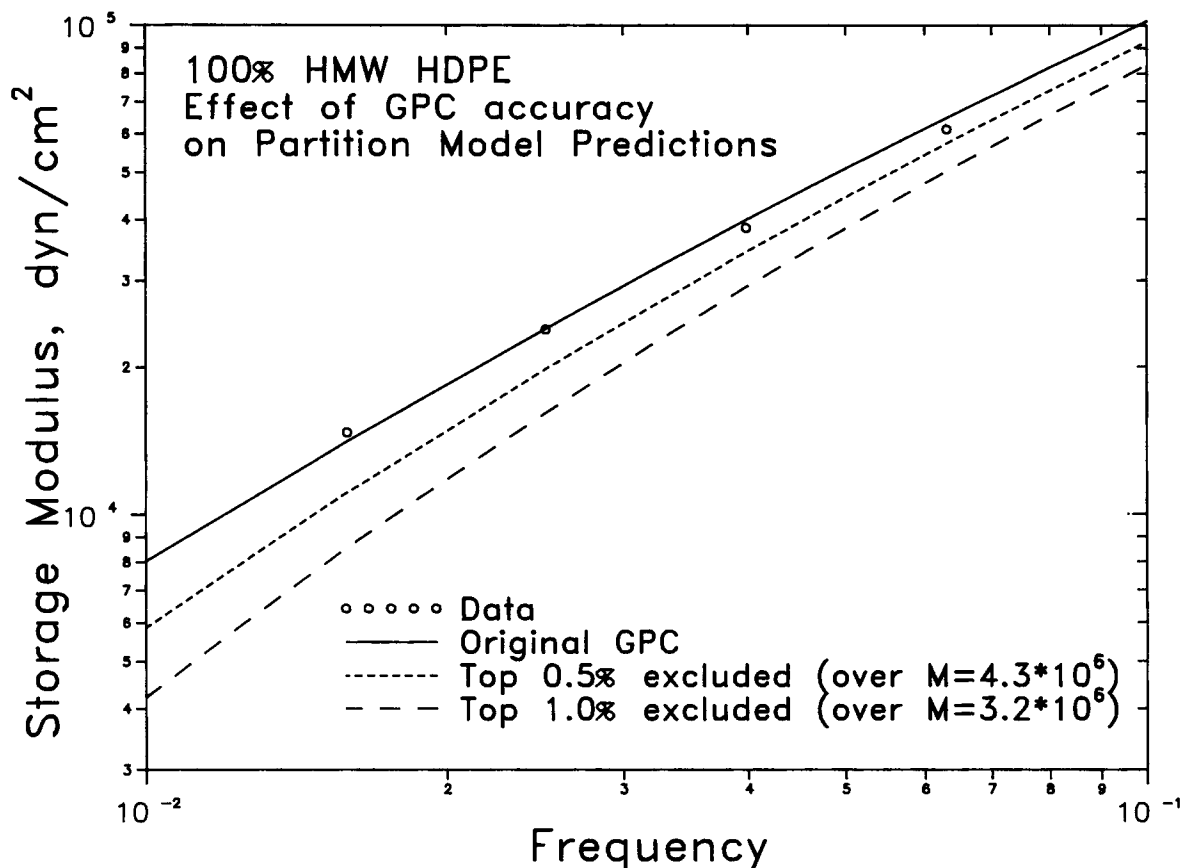


Figure 9 Effect of MWD errors (in the high MW tail) on the partition model predictions for storage modulus.

quencies. It is also interesting that the rheologically accessible elastic response (10^{-2} – 10^{-2} s⁻¹) is controlled completely by molecular weights larger than 50,000.

Interestingly, the picture is somewhat different for the loss modulus in Figure 12(b) (the viscous response). The trend is the same, i.e., the high mo-

lecular weights dominate the response at low frequencies. However, the greatest sensitivity to lower molecular weight contributions is displayed at high frequencies (observe the higher peak at higher frequencies, i.e., a smaller range of molecular weights contributes to G'' at high frequencies).

It is apparent from the above that the partition

Table III Effect of MWD Accuracy on Partition Model Predictions (HMW-HDPE)

	Original MWD	Top 0.5% Excluded (over MW = 4.3×10^6)	Top 1.0% Excluded (over MW = 3.2×10^6)
M_w (10^5)	4.144	3.893	3.730
M_w/M_n	5.020	4.730	4.560
M_z/M_w	3.530	2.860	2.640
η_0 (10^6 poise)	4.820	3.900	3.370
J_e^0 (10^{-6} cm ² /dyn)	31.500	8.010	5.320
G' ($\omega = 0.01$) (10^3 dyn/cm ²)	8.010	5.850	4.210

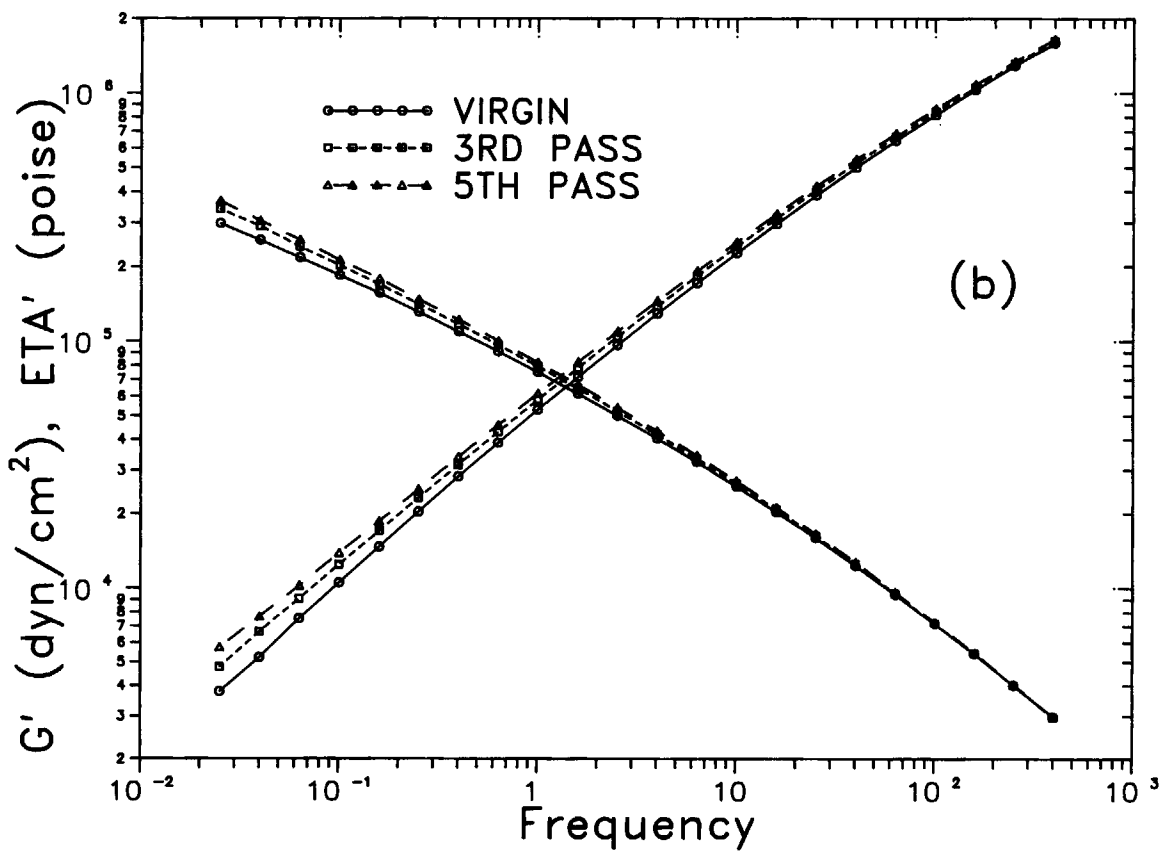
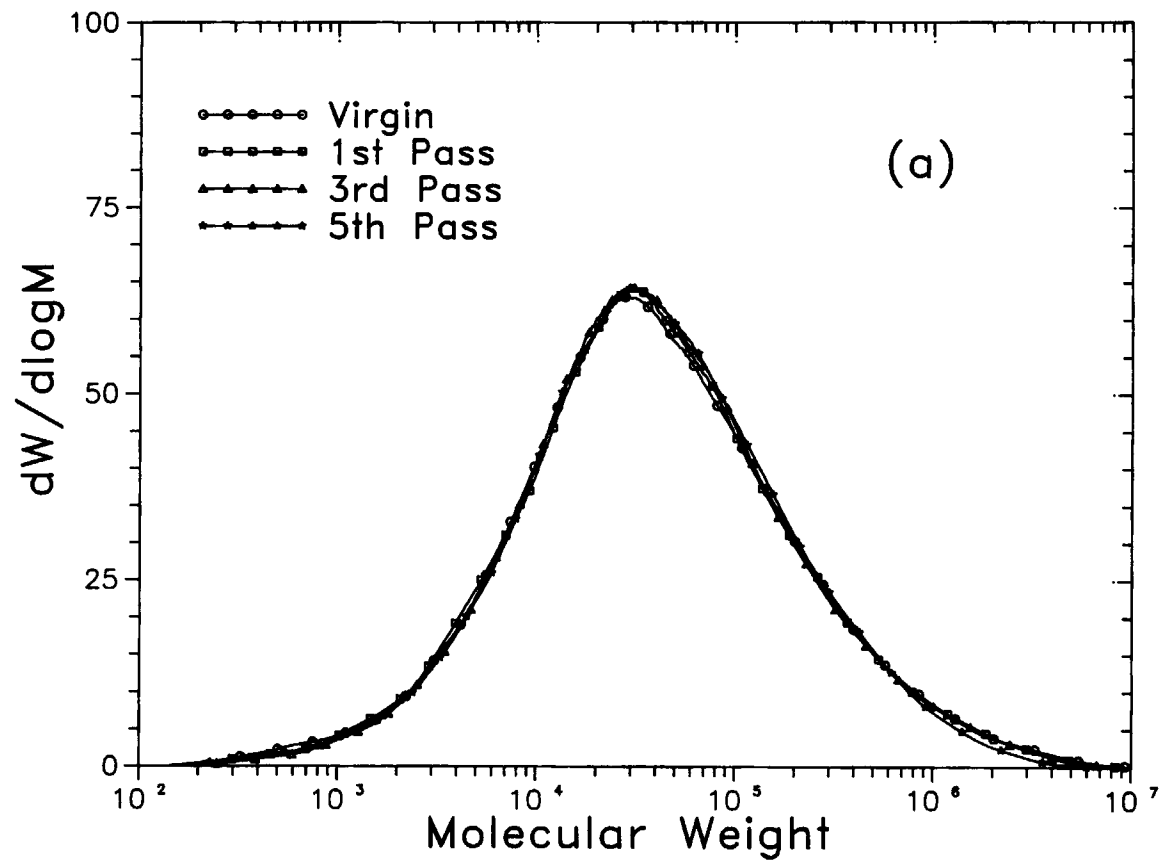


Figure 10 (a) GPC and (b) rheology data on an HDPE subjected to multiple-pass extrusion.

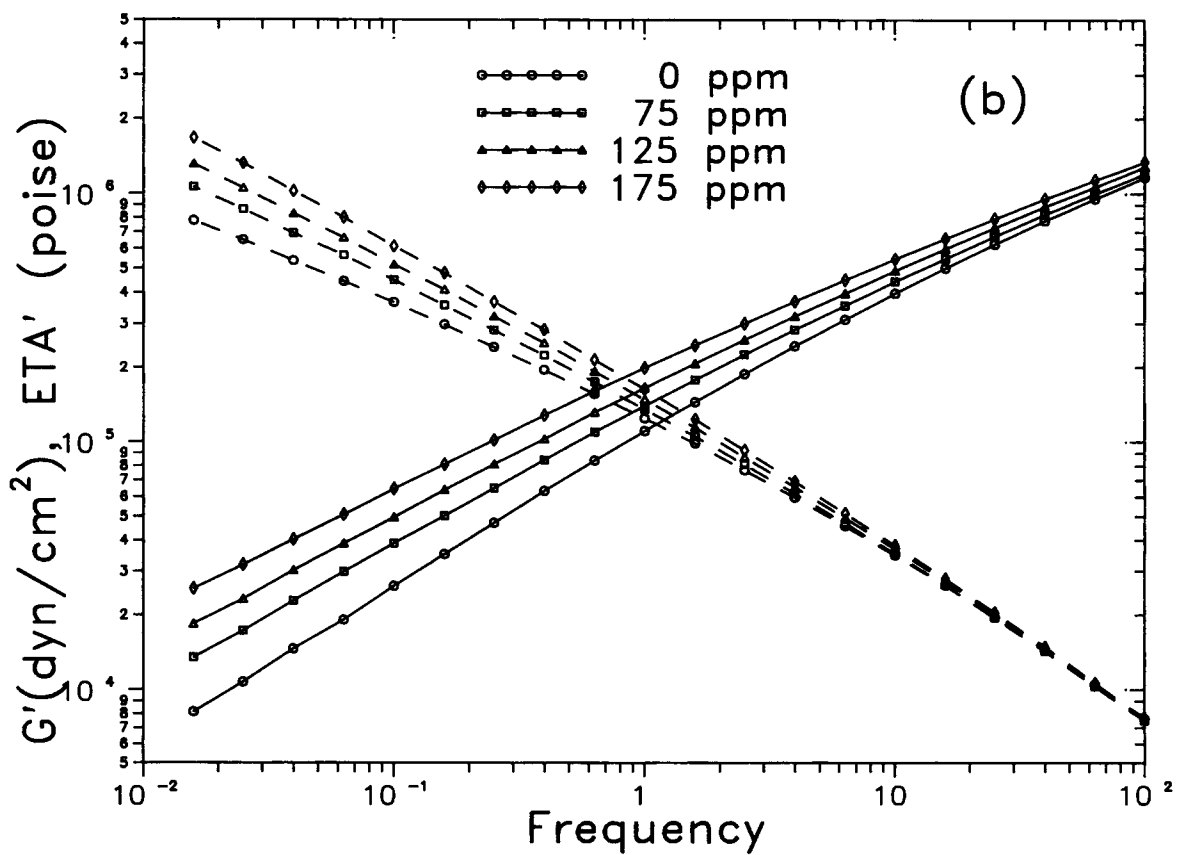
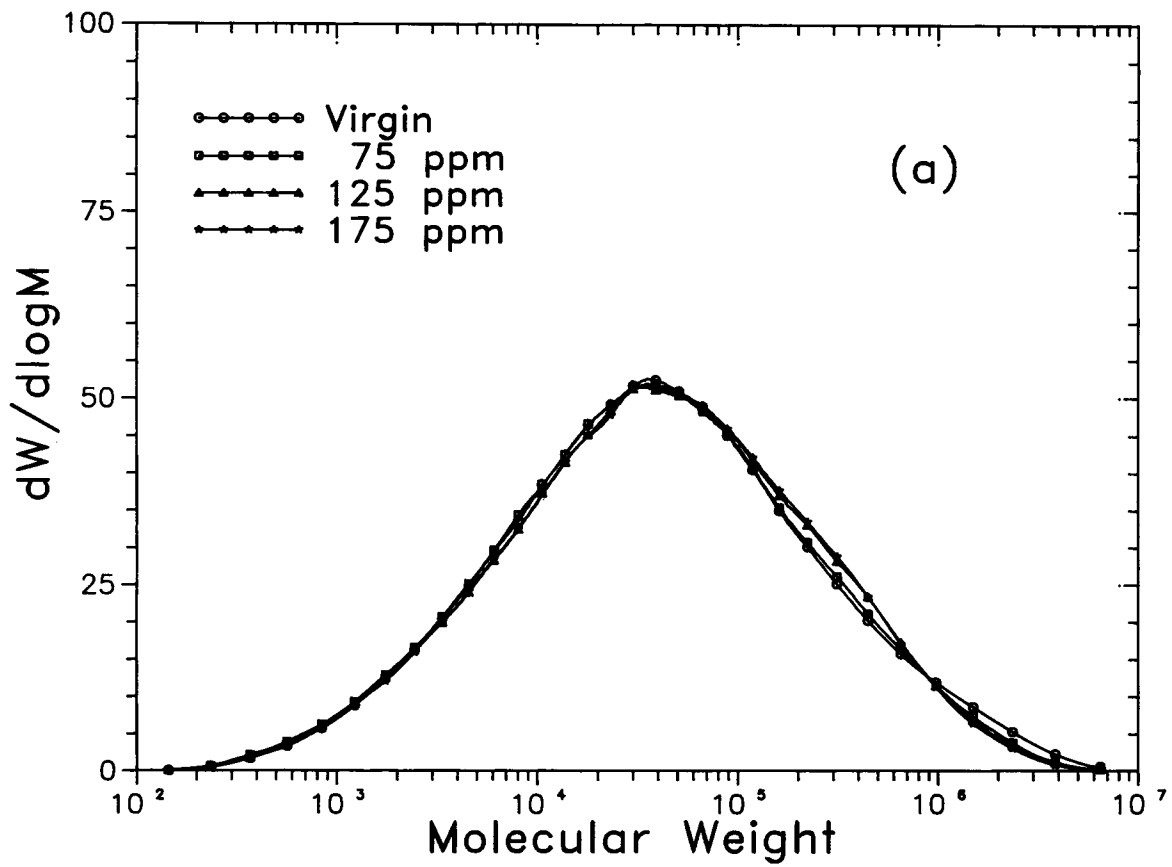


Figure 11 (a) GPC and (b) rheology data on an HDPE subjected to peroxide modification.

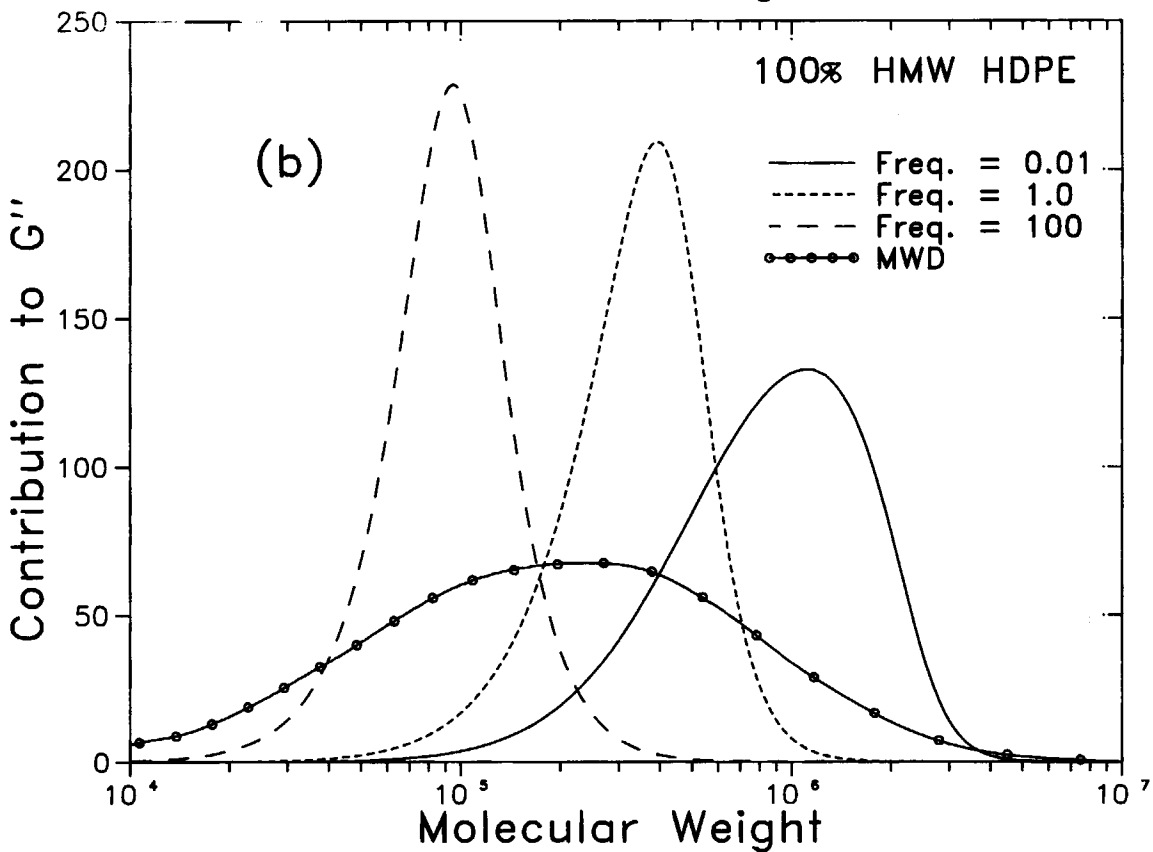
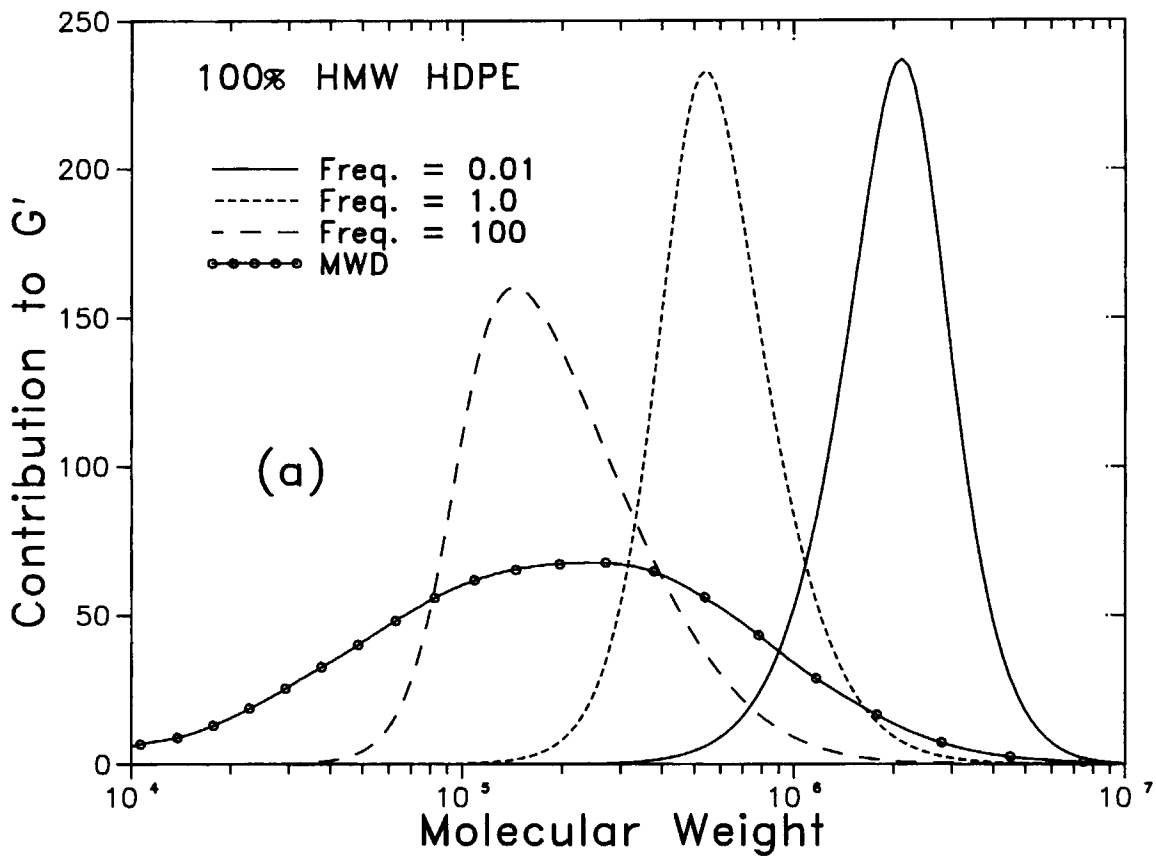


Figure 12 (a) Distribution plot of contributions of molecular weights to storage modulus at three frequencies for HMW-HDPE. MWD also plotted for reference purposes. (b) Distribution plot of contributions of molecular weights to loss modulus at three frequencies for HMW-HDPE. MWD also plotted for reference purposes.

model provides a valuable tool in discriminating among the contributions of molecular weights to rheological response and evaluating the relative sensitivity of the rheological functions. It is also noteworthy that the high molecular weight side of the molecular weight distribution dominates the rheological properties.

CONCLUDING REMARKS

The rheology of polymer melts depends strongly on the underlying molecular weight characteristics (MW and MWD). Establishing a quantitative relation between rheology and MWD would provide a structure-property link between polymer production and polymer processing.

The present work focused on interrelating rheology to MWD for linear polyolefins. Three sets of well-characterized data (a series of HDPE blends, a series of typical HDPEs, and a series of LLDPEs) were selected for testing purposes.

The partition model of Bersted was evaluated. This model is a four-parameter theory relating the linear viscoelastic relaxation spectrum to the MWD. The model did fit the data with better than 10% accuracy, but the fitted parameters showed some variability. An error analysis showed that the high sensitivity of rheology to molecular weight is responsible for the fact that errors in MWD are amplified strongly in the predicted rheological properties. The rheological properties are heavily influenced by the high molecular weight tail of the MWD. Errors in MWD determination are detrimental for an MWD-to-rheology conversion, even if the conversion scheme were perfectly accurate. Also, the presence of small levels of long-chain branching in an otherwise linear polymer alters the rheology dramatically. It is not clear at present how to account for LCB in the MWD-to-rheology conversion scheme.

The inverse problem, determination of MWD from rheology, is addressed in the Appendix. It is noted that in the rheology-to-MWD conversion, the errors are attenuated (rather than amplified, as in the MWD-to-rheology conversion). However, the conversion is practically infeasible for commercial polymer melts due to the incompleteness of the experimentally accessible rheological data. The experimentally accessible rheological information is less than half the complete range that is required for the conversion, whereas in the MWD-to-rheology conversion, one has full MWD information (up to the exclusion limits of the size exclusion chroma-

tography columns). Note that the infeasibility of the rheology-to-MWD conversion is independent of the validity of the partition model, and it merely reflects experimental limitations.

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APPENDIX: DETERMINATION OF MWD FROM RHEOLOGY

A theory relating MWD to rheology can, in principle, be inverted to yield MWD from rheology. Let the differential molecular weight distribution be $w(\ln M)$:

$$\int_{-\infty}^{+\infty} w(\ln M) d \ln M = 1 \quad (\text{A.1})$$

The cumulative molecular weight distribution $\phi(\ln M)$ is

$$\phi(\ln M) = \int_{-\infty}^{\ln M} w(\ln M') d \ln M' \quad (\text{A.2})$$

The effective weight-average molecular weight is

$$M_w^*(M_c) = \int_{-\infty}^{\ln M_c} M w(\ln M) d \ln M + M_c \int_{\ln M_c}^{+\infty} w(\ln M) d \ln M \quad (\text{A.3})$$

Differentiating eq. (A.3) once:

$$\phi(\ln M_c) = 1 - \frac{\partial M_w^*}{\partial M_c} \quad (\text{A.4})$$

Differentiating eq. (A.3) twice:

$$w(\ln M_c) = - \frac{\partial}{\partial \ln M_c} \frac{\partial M_w^*}{\partial M_c} \quad (\text{A.5})$$

Using eqs. (6) and (7) in eqs. (A.4) and (A.5), we finally have

$$\phi(\ln M_c) = 1 - \frac{M_w^*}{M_c} \frac{\alpha_2}{\alpha_1} \frac{\partial \ln \eta_0}{\partial \ln \tau_c} \quad (\text{A.6})$$

$$w(\ln M_c) = \frac{M_w^*}{M_c} \frac{\alpha_2}{\alpha_1} \left[- \frac{\alpha_2}{\alpha_1} \left(\frac{\partial \ln \eta_0}{\partial \ln \tau_c} \right)^2 + \frac{\partial \ln \eta_0}{\partial \ln \tau_c} - \alpha_2 \frac{\partial^2 \ln \eta_0}{\partial \ln^2 \tau_c} \right] \quad (\text{A.7})$$

$$M_c(\tau_c) = \left(\frac{\tau_c}{k_2} \right)^{1/\alpha_2} \quad (\text{A.8})$$

$$M_w^*(\eta_0) = \left(\frac{\eta_0}{k_1} \right)^{1/\alpha_1} \quad (\text{A.9})$$

$$\eta_0(\tau_c) = \int_0^{\tau_c} H(\tau) d\tau \quad (\text{A.10})$$

The procedure to compute the MWD from rheology would be

Required data: Complete relaxation spectrum $H(\tau)$
Material parameters k_1 , α_1 , k_2 , and α_2 .

For every relaxation time $\tau_i = i \cdot \Delta\tau$, where $\Delta\tau$ is a relaxation time increment, do the following:

- Step 1:* Calculate corresponding molecular weight M_i from eq. (A.8).
- Step 2:* Calculate viscosity $\eta_0(\tau_i)$ from eq. (A.10) and the first and second derivatives with respect to relaxation time [to be used in eq. (A.7)].
- Step 3:* Calculate M_w^* from eq. (A.8).
- Step 4:* Substitute in eq. (A.6) to calculate the cumulative MWD $\phi(\ln M_i)$.
- Step 5:* Substitute in eq. (A.7) to calculate the differential MWD $w(\ln M_i)$.

The fundamental problem with the above procedure is that it requires the relaxation spectrum over the full range of relaxation times. An example with a commercial HDPE will help reinforce the point. Consider HDPE-2, a typical HDPE, whose MWD as measured by GPC extends from 10^3 to 10^7 in molecular weight. Using the constants $\log_{10} k_2 = -16.65$ and $\alpha_2 = 2.905$ from Table II, we find from eq. (A.8) that the equivalent (i.e., full) range of relaxation times is from 10^{-8} to 10^4 s, i.e., *12 decades of relaxation time*. The rheologically accessible range for this material was $0.063\text{--}400$ s⁻¹ in frequency (linear viscoelastic data). From these frequency data, the linear viscoelastic relaxation spectrum can be computed over *6–7 decades of relaxation time* at best,¹⁹ i.e., the rheological data are incomplete almost by half.

It is this incompleteness of the rheological data that render the rheology-to-MWD conversion practically infeasible for commercial polymer melts. Note that extracting some polydispersity measure from rheological data is still possible (see, e.g., Refs. 20–22). However, the com-

plete MWD is unlikely to be obtained from rheology for all but extremely narrow distribution polymers.

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