

New Measures of Polydispersity from Rheological Data on Polymer Melts

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SYNOPSIS

The rheological properties of polymer melts depend strongly on the underlying molecular structure: molecular weight, molecular weight distribution, and long chain branching. It is of considerable importance, both fundamental and practical, to relate the molecular architecture to polymer melt rheology. The focus of the present work is in extracting a measure of polydispersity from rheological data. Various polydispersity measures that have been proposed in the literature are critically examined and their limitations are pointed out. New measures of polydispersity are proposed that overcome these limitations. The evaluation of the various polydispersity measures is performed by reference to rheology fundamentals, with model calculations and examples drawn from industrial practice. The issues of eliminating molecular weight and temperature effects in characterizing polydispersity are comprehensively addressed. The presence of small levels of long chain branching in an otherwise linear polymer alters most of these measures of polydispersity dramatically, while no detectable change appears in the molecular weight distribution obtained using a gel permeation chromatograph. It is demonstrated that the polydispersity measures proposed in the present work, and which are extracted from frequency response data in the linear viscoelastic region, can be used reliably to characterize polydispersity in polymer melts. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that the rheological properties of polymer melts depend strongly on the underlying molecular structure; specifically, molecular weight, molecular weight distribution (MWD), and long chain branching (LCB).¹ In recent years, there has been considerable interest in this area relating the melt rheology of a polymer to its molecular architecture. Several publications appeared attempting to predict the rheological properties given a molecular weight distribution and, possibly, vice versa.²⁻¹¹ Despite the subject's obvious importance and its long history, several key issues remain unsettled and work in this area continues actively.¹²

Aside from the fundamental interest in relating molecular architecture to polymer melt rheology, there are practical reasons for it in industrial practice having to do with polymer product development, catalyst and/or process development, material characterization, and quality control. For example, the MWD of a polymer plays a critical role in end-use properties. Control of the MWD would require means of MWD monitoring that offer reliable, accurate, and rapid measurement. Rheological measurements provide an attractive candidate in this regard, provided the MWD information can be extracted from the rheological data.

The present authors have also addressed the issue of interconversion between rheological properties and MWD in linear polymers (specifically, polyolefins).¹¹ In that work, a conversion scheme was described for the prediction of the linear viscoelastic properties of a polymer melt from the MWD. The MWD was determined by Gel Permeation Chromatography (GPC). It was shown that rheological properties have a pronounced sensitivity to molec-

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Journal of Applied Polymer Science, Vol. 57, 1605-1626 (1995)
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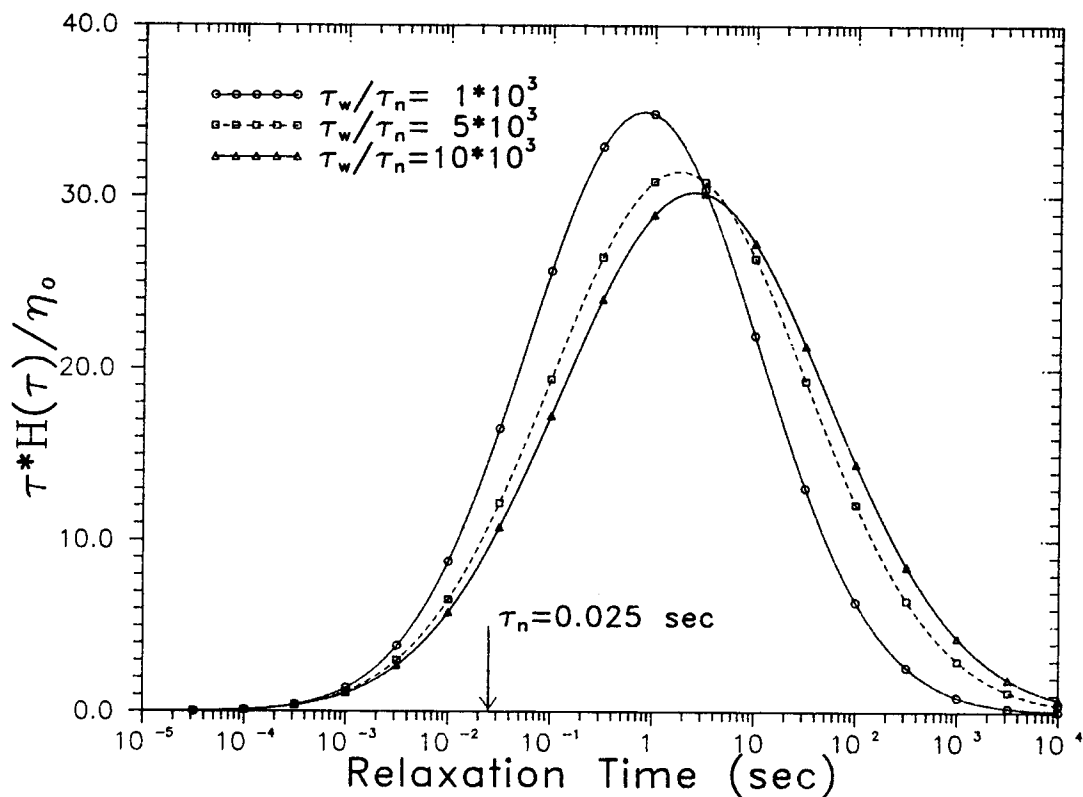


Figure 1 Model relaxation spectra (log-normal distributions).

ular weight and MWD. This sensitivity causes error amplification in the MWD-to-Rheology conversion. Consequently, errors that are largely unavoidable and inherently present in solution measurements such as GPC are amplified and contaminate the predicted rheological response, even if the conversion scheme were perfectly accurate (in fact, the sensitivity of rheology to MW and MWD may impede the development of interconversion schemes by making model validation difficult, because experimental error may be confounded with model inadequacies).

The inverse problem of determining the MWD from the rheological data is more difficult. Whereas in the MWD-to-Rheology conversion one generally starts with the complete MWD information, in the inverse Rheology-to-MWD problem, the rheological data are almost never complete (due to instrumental limitations). In fact, for commercial, broad MWD polyethylenes it was shown in ref. 11 that the rheological data are incomplete by half (in terms of the accessible shear rate or frequency range). This incompleteness, combined with the general ill-posed nature of inverse problems in Rheology,¹³ makes infeasible the Rheology-to-MWD conversion for all but very narrow MWD polymers.

It was mentioned in ref. 11 that, even though one may not be able to obtain the complete MWD from rheological data, extracting some polydispersity measure from the rheological data is possible and desirable. It is the subject of this article to review the available approaches for extracting molecular weight polydispersity measures from rheological data and propose some new ones.

BACKGROUND

The Melt Index test (ASTM D-1238) provides a rheological measurement that has long been used for polymer characterization. This test measures the "flow rate" in grams per 10 min of polymer flowing through a die at a given temperature under the action of a weight loaded onto a piston. Typical test conditions are 190/2.16, i.e. 190°C temperature and 2.16 kg weight, in which case the "flow rate" is known as "Melt Index" (MI). More details about the test are given in refs. 14-17.

Measuring the flow rate in the Melt Indexer under various load weights corresponds (roughly) to measuring shear viscosities at different shear stresses. For example, measuring the flow rate at 190/21.6

(190°C and 21.6 kg weight) gives what is known as HLMI in polyethylene (High-Load Melt Index). Having the two values of Melt Index (MI) and High-Load Melt Index one can then take the ratio HLMI/MI, which is used in industrial practice as a measure of polydispersity.¹⁸ Measuring the flow rate at other load weights and taking the ratio is also used as a polydispersity measure. An example is the I10/I2 ratio (load weights of 10 kg and 2.16 kg).

The justification of using ratios of melt flow rates at different load weights as a polydispersity measure comes from the realization that these ratios essentially characterize the degree of shear thinning or shear sensitivity of the polymer. The degree of shear sensitivity, in turn, is directly associated with the breadth of the molecular weight distribution, with broad MWD resulting in more shear sensitive viscosity behavior.

Graessley¹⁹ developed a theory that relates the MWD of a linear polymer to the shear viscosity curve. Graessley's model does predict a higher shear sensitivity for a broader MWD and did have some success in predicting the shape of the viscosity–shear rate curves from information on the MWD.^{1,20}

Graessley²³ also developed experimentally the following relation, which is reported to seem universal for entangled polymers:

$$\eta_0 \dot{\gamma}_0 J_e^0 = 0.6 \pm 0.2 \quad (1)$$

where η_0 is the zero-shear viscosity, $\dot{\gamma}_0$ is a characteristic shear rate (defined as the shear rate at which the viscosity decreases to $0.8\eta_0$), and J_e^0 is the steady-state compliance.

While Graessley's theory provides justification for using a shear viscosity sensitivity index as a measure of molecular weight polydispersity, the limitations of using melt index ratios, such as HLMI/MI, for shear sensitivity have long been recognized. Shida and Cancio¹⁸ noted that differences in shear sensitivity between two polymers may manifest themselves at shear stresses lower than that used in the melt indexer and, thus, go undetected by the HLMI/MI ratio. Shida and Cancio¹⁸ also noted that the shear sensitivity as characterized by melt index ratios shows a dependence on molecular weight level, which is undesirable.

Shida and Cancio¹⁸ proposed a measure of polydispersity derived from capillary viscosity data. Specifically, they fitted capillary data of viscosity, η , vs. shear rate, $\dot{\gamma}$, to the Sabia equation:²¹

$$\ln\left(\frac{\eta}{\eta_0}\right) = \left(\frac{\eta}{\eta_0} - A\right) \cdot \ln\left[1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right)^B\right] \quad (2)$$

where the values A , B were fixed at $A = 2$ and $B = \frac{1}{3}$ for polyethylene (the A -value was later allowed free to fit to data). A polydispersity measure, called R_D , was then defined as:¹⁸

$$R_D = \frac{3 \cdot 10^6}{\eta_0 \dot{\gamma}_0^s} \quad (3)$$

where $s = 0.75$ and η_0 is in units of poise. Note that $\dot{\gamma}_0$ in eqs. (2) to (3) above is different from $\dot{\gamma}_0$ in Graessley's correlation, eq. (1). Graessley's $\dot{\gamma}_0$ is defined at $\eta/\eta_0 = 0.8$, whereas in Sabia's equation, $\dot{\gamma}_0$ depends on the A value. For $A = 2$, it turns out that $\dot{\gamma}_0$ is at $\eta/\eta_0 = 0.31$. R_D has also been used to characterize polydispersity in LDPE.²²

It will be shown later that the proper exponent in eq. (3) should be $s = 1.0$ for linear polyethylenes, in which case combining eq. (3) and eq. (1) gives (bypassing the difference in $\dot{\gamma}_0$ definition at the moment):

$$R_D \sim J_e^0 \quad (4)$$

and, therefore, the fundamental justification of R_D is that it is proportional to the steady-state compliance. It is well known that the steady-state compliance is independent of molecular weight but depends strongly on MWD, particularly the high molecular weight tail.²³

Another measure of polydispersity that has been used in the past is the extrudate swell at a given level of shear stress; the broader the MWD, the higher the extrudate swell.¹ This result can also be related to the steady-state compliance. For long dies, Tanner's expression for extrudate swell gives:²⁴

$$\text{Extrudate Swell} = \left[1 + \frac{1}{8} \left(\frac{N_1}{\sigma}\right)^2\right]^{1/6} \quad (5)$$

As noted by Graessley,¹ $N_1 \sim 2 J_e^0 \sigma^2$ and, therefore, at a given shear stress, σ , the extrudate swell will increase with increasing J_e^0 . Note, however, that this analysis is limited to long dies. For short dies, there is significant entrance flow memory effect. Also, the degree of extrudate swell is affected by extrudate cooling and sagging, which are difficult to account for rigorously and complicate the picture.

Shida et al.²² and Pucci and Shroff²⁵ have used a plot of entrance pressure drop vs. shear stress to differentiate MWD and long chain branching effects.

Zeichner and Patel²⁶ proposed a polydispersity index derived from frequency data in the linear viscoelastic region. Their polydispersity index, PI , is:

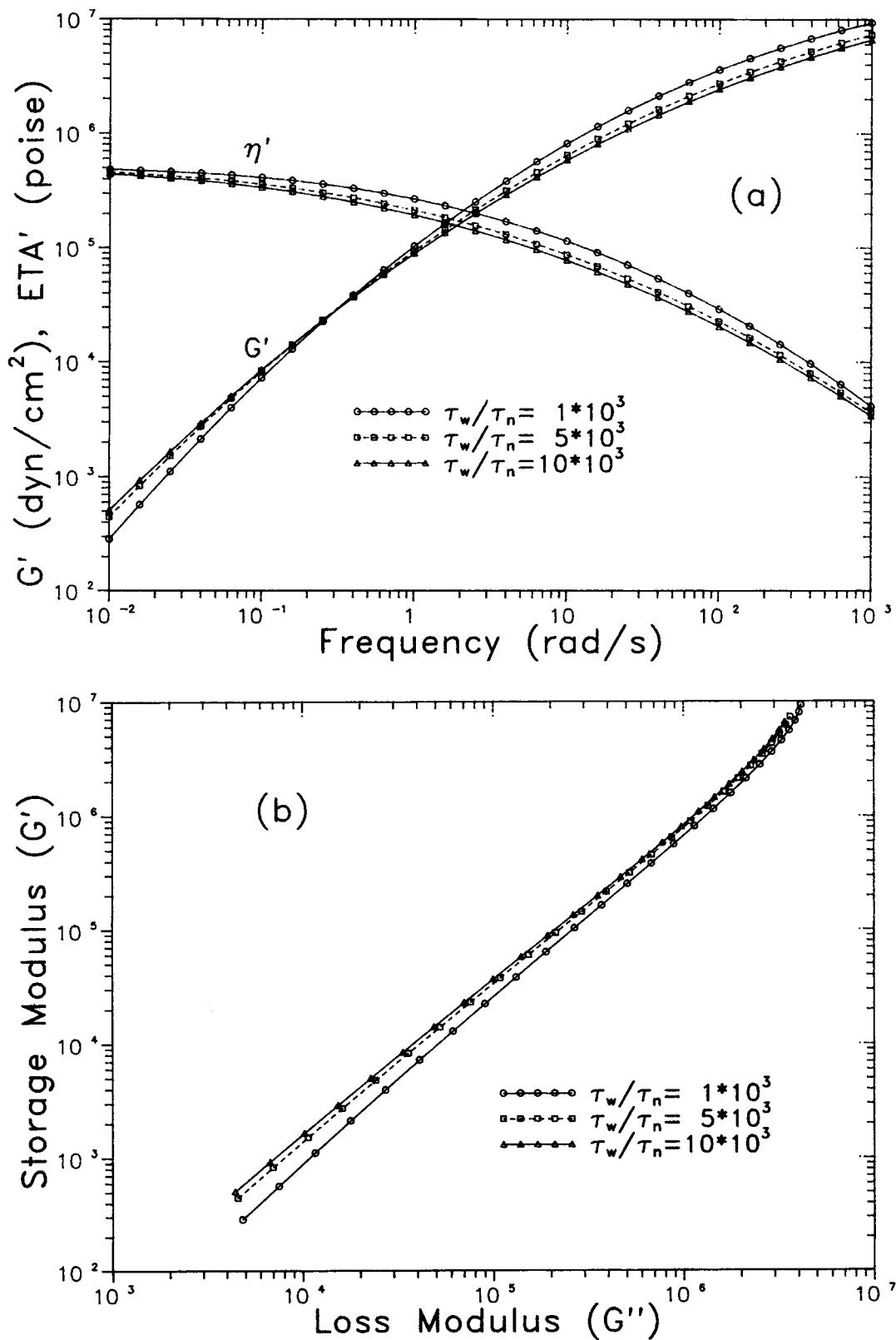


Figure 2 Linear viscoelastic data derived from the spectra of Figure 1. (a) Storage modulus and dynamic viscosity vs. frequency; (b) storage modulus vs. loss modulus; (c) loss tangent vs. complex modulus.

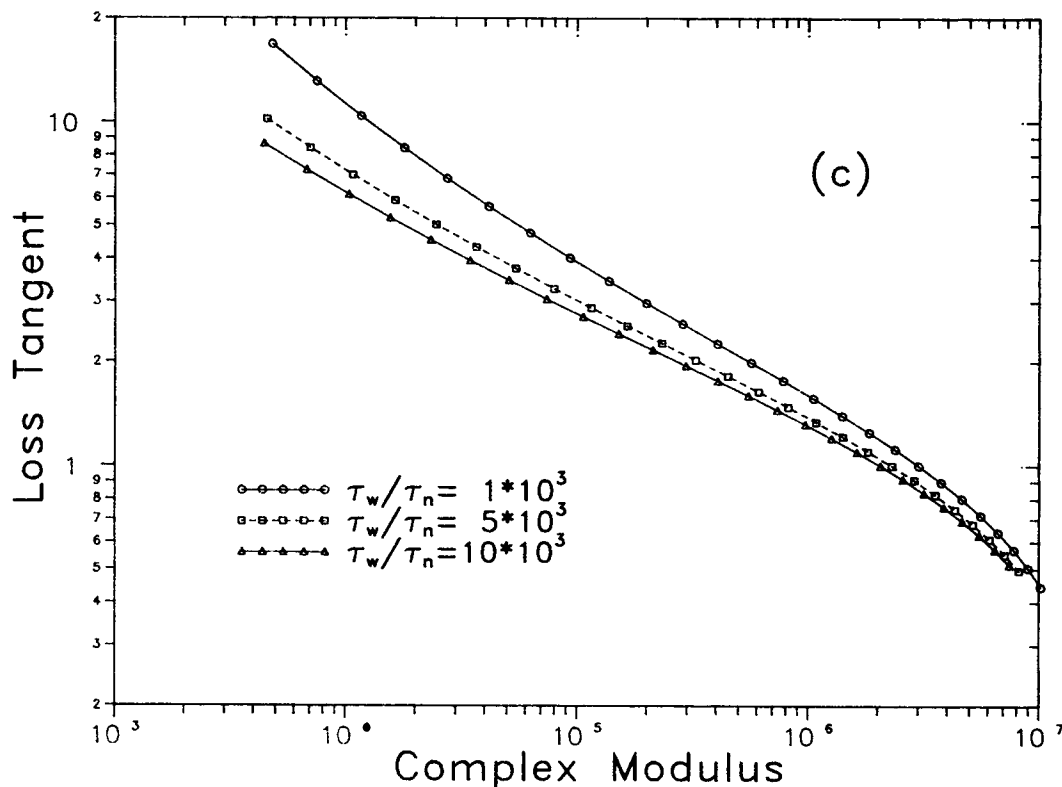


Figure 2 (Continued from the previous page)

$$PI = \frac{10^6 \text{ dyn/cm}^2}{G_c} \quad (6)$$

where G_c is the crossover modulus. Zeichner and Macosko²⁷ reported good correlation between PI and $M_w/M_n, M_z/M_w$ for polypropylenes. The fundamental basis for PI is not immediately obvious. Some further comments on PI are given later.

Han and Lem²⁸ proposed several choices of plotting rheological properties of polymer melts so as to get temperature independent curves that can be used to compare the elastic properties in a relative sense: plots of N_1 (or S_R or J_e) vs. σ_w , or plots of G' [or $\tan\delta$ or $G'/(G'')^2$] against G'' .

Harrell and Nakajima²⁹ proposed the use of the so-called modified Cole-Cole plot for characterizing polydispersity. The method involves plotting G' vs. G'' in logarithmic coordinates and recognizes the fact that the relative value of G' over that of G'' at low frequencies is affected by MWD and long chain branching.

Recently, Yoo³⁰ proposed the use of the "Modulus Separation" (Modsep) to characterize polydispersity in polypropylene. According to Yoo,³⁰ the Crossover modulus technique of Zeichner and Patel²⁶ is limited to polypropylenes of Melt Flow Rate (MFR) less

than 40 [this limitation is probably due to the fact that for high MFR resins the crossover frequency falls outside the experimentally accessible range (< 500 rad/s)]. The modulus separation is defined as:³⁰

$$\text{Modsep} = \frac{\omega'}{\omega''}$$

ω' : Frequency at $G' = G_{\text{ref}}$

ω'' : Frequency at $G'' = G_{\text{ref}}$ (7)

where G_{ref} is 10,000 dyn/cm² for MFR < 100, 5000 dyn/cm² for 100 < MFR < 1000, and 1000 dyn/cm² for MFR > 1000.

Another polydispersity measure derived from rheological data has also been proposed very recently by Lai et al.³¹ Lai's measure is derived from shear viscosity vs. shear rate data, which are fitted to a Cross viscosity equation:

$$\frac{\eta}{\eta_o} = \frac{1}{1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_o}\right)^{1-n}} \quad (8)$$

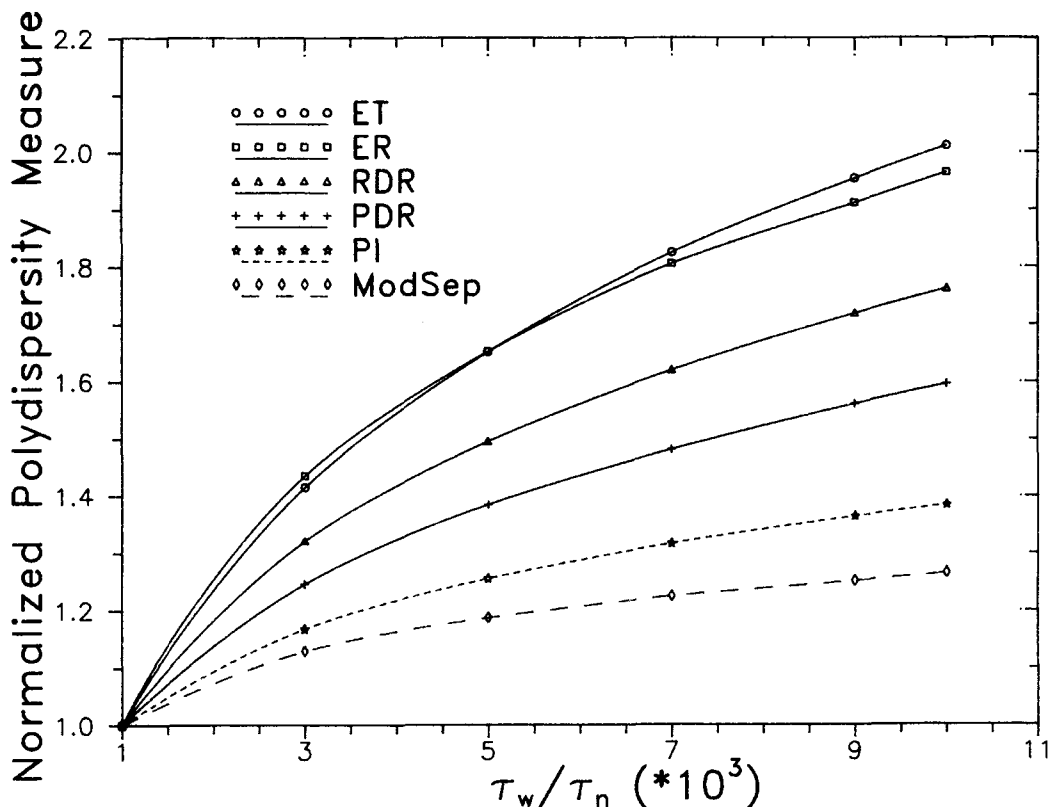


Figure 3 Normalized polydispersity measures vs. relaxation spectrum polydispersity.

When linear viscoelastic data are used the complex viscosity η^* is used instead of the steady-shear viscosity η , and the frequency ω is used instead of the shear rate. The polydispersity measure, called *DRI*, is defined as:

$$DRI = \frac{3.56 \cdot 10^5}{\eta_0 \cdot \dot{\gamma}_0} - 0.1 \quad (9)$$

DRI was introduced to characterize the level of long chain branching for the INSITE family of polyolefins made by Dow Chemical. These polymers have very narrow MWD ($M_w/M_n \sim 2$) and, consequently, differences in rheologically measured polydispersity can be ascribed to long chain branching (otherwise, if both MWD and long chain branching were changing, there would be no simple method to separate the two effects).

Comparison of eq. (9) and eq. (3) shows that the *DRI* is almost identical in concept to R_D . In fact, *DRI* lacks some of the flexibility of R_D , as will be shown later.

It is instructive to search for a fundamental justification of the various polydispersity measures derived from the linear viscoelastic data, particularly

the frequency response. The storage and loss moduli are defined as:

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

$$G''(\omega) = \int_{-\infty}^{+\infty} H(\tau) \frac{(\omega\tau)}{1 + (\omega\tau)^2} d \ln \tau \quad (10)$$

In the limit of low frequencies (or low moduli) the asymptotic behavior is:

$$G'(\omega) = \eta_0^2 J_e^0 \omega^2 \quad \text{for } \omega \rightarrow 0$$

$$G''(\omega) = \eta_0 \omega \quad \text{for } \omega \rightarrow 0 \quad (11)$$

where η_0 is the zero shear viscosity and J_e^0 is the compliance:

$$\eta_0 = \int_{-\infty}^{+\infty} H(\tau) \tau d \ln \tau$$

$$J_e^0 = \frac{1}{\eta_0^2} \int_{-\infty}^{+\infty} H(\tau) \tau^2 d \ln \tau \quad (12)$$

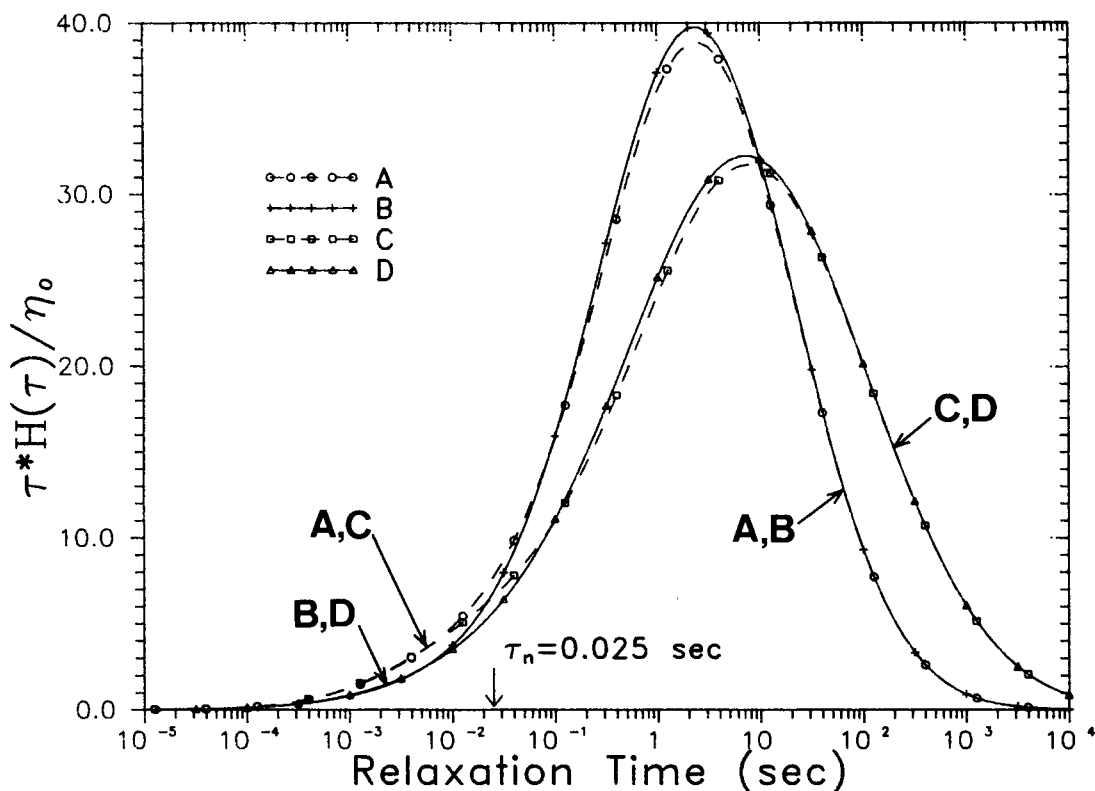


Figure 4 Nonsymmetric model relaxation spectra.

Note also that the number- and weight-average relaxation times are given from:

$$\tau_n = \frac{\int_{-\infty}^{+\infty} H(\tau)\tau d \ln \tau}{\int_{-\infty}^{+\infty} H(\tau) d \ln \tau} = \frac{\eta_0}{G_N^0}$$

$$\tau_w = \frac{\int_{-\infty}^{+\infty} H(\tau)\tau^2 d \ln \tau}{\int_{-\infty}^{+\infty} H(\tau)\tau d \ln \tau} = \eta_0 \cdot J_e^0 \quad (13)$$

and, therefore, a polydispersity of the relaxation spectrum can be defined as:

$$\frac{\tau_w}{\tau_n} = J_e^0 \cdot G_N^0 \quad (14)$$

From eq. (11) we can write the characteristic frequencies ω' and ω'' as:

$$\omega' = \left(\frac{G'}{\eta_0^2 J_e^0} \right)^{1/2}, \quad \omega'' = \left(\frac{G''}{\eta_0} \right) \quad (15)$$

Table I Comparison of Polydispersity Index Values for Model Spectra

Model Spectrum	τ_n/τ_H	τ_w/τ_n	τ_z/τ_w	PI	Mod Sep	ER	ET	RDR ^a	PDR
Spectrum A	10 ³	10 ³	130	0.89	4.8	0.82	1.6	2.4	5.4
Spectrum B	10 ⁴	10 ³	130	1.4	4.7	0.82	2.1	3.4	6.4
Spectrum C	10 ³	10 ⁴	1300	0.63	3.9	1.6	2.0	2.6	6.7
Spectrum D	10 ⁴	10 ⁴	1300	1.2	3.8	1.6	3.3	3.9	8.6

^a AB = 0.72, A = 2, s = 1.0.

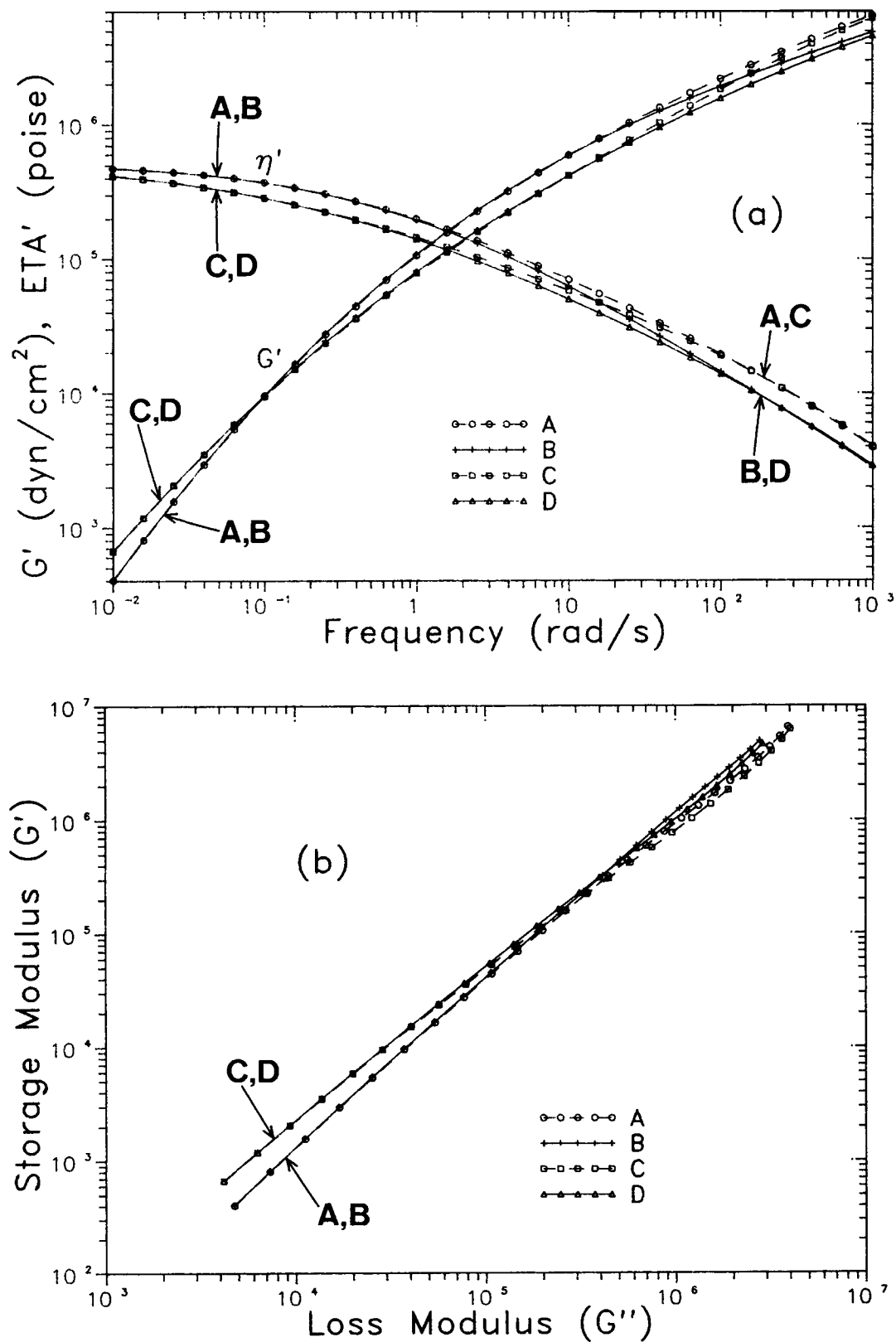


Figure 5 Linear viscoelastic data derived from the spectra of Figure 4. (a) Storage modulus and dynamic viscosity vs. frequency; (b) storage modulus vs. loss modulus; (c) loss tangent vs. complex modulus.

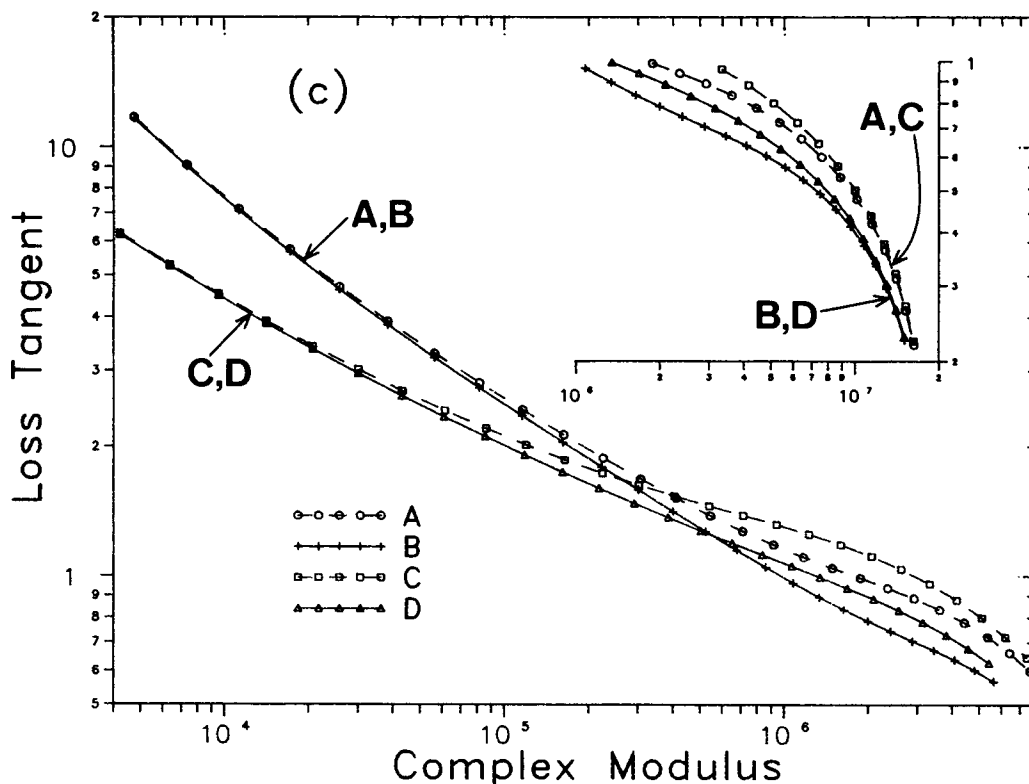


Figure 5 (Continued from the previous page)

Substituting eq. (15) into eq. (7) for Yoo's Modulus Separation, and noting that $G' = G'' = G_{ref}$, we get:

$$\text{Modsep} = (G_{ref} \cdot J_e^o)^{-1/2} \quad (16)$$

Equation (16) justifies Yoo's³⁰ Modsep as a polydispersity index because the compliance J_e^o is a polydispersity measure [see eq. (14)]. The plateau modulus G_N^o is constant for a given polymer type. Note that the above treatment is strictly valid in the asymptotic limit of low frequencies. This limit may not be accessible experimentally, in which case one should opt for the lowest frequency possible or, equivalently, the lowest modulus value accessible experimentally (low G_{ref}).

Similarly, from eq. (11) we get:

$$G'(\omega) = J_e^o [G''(\omega)]^2 \quad \text{for } \omega \rightarrow 0 \quad (17)$$

Eq. (17) justifies Harrell and Nakajima's²⁹ modified Cole-Cole plot. The level of G' at low G'' can, indeed, be taken as a measure of polydispersity because it is proportional to the steady-state compliance [eq. (17)]. Again, eq. (17) is valid in the low-frequency (terminal) region where the asymp-

totic relationship eq. (11) holds. However, these asymptotic relations are very helpful in providing justification for the various polydispersity indexes, as well as comparing the various indexes. Thus, the Modulus Separation is expected to have half the sensitivity of the modified Cole-Cole plot, as evidenced from eqs. (16) and (17) [the Modsep in eq. (16) is proportional to the 1/2 power of J_e^o , whereas the G' in eq. (17) is proportional to the first power of J_e^o].

Therefore, we conclude that most polydispersity measures derived from rheological data that have been reported in the literature can be justified by association to the steady-state compliance J_e^o , which in itself is proportional to the relaxation time polydispersity τ_w/τ_n [eq. (14)]. The only exception is the crossover modulus [eq. (6)], which, by numerical experiments, can be shown to be related to lower moments of the relaxation spectrum.

NEW MEASURES OF POLYDISPERSITY

The requirements of a polydispersity index derived from rheological data are:

Table II Comparison of Polydispersity Index Values for Commercial Linear Polyolefins

Polymer	PI	Mod Sep	ER	ET	RDR ^a	PDR
LMW-HDPE	0.63	5.5	0.85	1.6	2.0 ^b	3.1
5% HMW	0.65	4.0	1.9	1.9	4.1 ^b	5.4
10% HMW	0.89	3.3	2.5	3.3	5.8 ^b	9.0
15% HMW	1.2	3.2	2.4	5.2	7.4 ^b	12.3
20% HMW	1.7	3.2	2.3	6.0	8.7 ^b	14.5
40% HMW	2.0	3.5	1.9	4.9	5.7 ^b	12.4
70% HMW	1.3	3.0	1.6	2.4	3.3 ^b	6.3
HMW-HDPE	0.84	3.2	0.95	1.3	2.1 ^b	4.0
HDPE-1	2.6	3.0	2.8	9.7	5.9 ^c	22.7
HDPE-2	2.2	3.0	2.8	8.9	5.2 ^c	20.2
HDPE-3	1.5	3.1	2.7	5.3	3.1 ^c	12.9
LLDPE-1	0.8	6.0	0.65	1.1	1.5 ^b	3.5
LLDPE-2	0.7	6.1	0.56	1.0	1.3 ^b	3.2
LLDPE-3	0.6	6.5	0.55	0.9	1.1 ^b	2.8
LLDPE-4	0.6	6.0	0.58	1.2	1.4 ^b	3.0

^a AB = 0.72, s = 1.0.

^b A = 2.

^c A = 3.

1. Ability to quantify polydispersity.
2. Ability to differentiate and discriminate higher from lower molecular weight contributions.
3. Independence of molecular weight. The polydispersity index should reflect molecular weight distribution irrespective of the actual level of molecular weight.
4. Independence of measurement temperature. The polydispersity index values derived from rheological data measured at different temperatures should be the same (unless material structure changes at different temperatures).
5. Accessibility and versatility. The required rheological data should be readily accessible with conventional instruments. The polydispersity index should also be widely applicable on the polymers of interest with minimum restrictions.
6. Sensitivity and robustness. The polydispersity index should be sensitive enough to quantify differences among materials, yet robust enough to experimental error.

The above requirements are best examined in terms of linear viscoelastic data. For the case of frequency response data (G' , G'' vs. ω), inspection of eq. (10) shows that the molecular weight and temperature influence the rheological properties through their effect on relaxation time and modulus. For well entangled polymer melts, the modulus is independent of molecular weight:

$$\int_{-\infty}^{+\infty} H(\tau) d \ln \tau \equiv G_N^0 = \frac{\rho RT}{M_e} \quad (18)$$

where M_e is the molecular weight between entanglements, ρ is the melt density, R is the gas constant, and T is the absolute temperature.

Therefore, any polydispersity measure derived from rheological data in such a way that the relaxation time is eliminated and only moduli are involved will be independent of molecular weight. This is the case of plotting G' vs. G'' (the modified Cole-Cole plot),²⁹ or plotting loss tangent (G''/G') vs. complex modulus [$G^* = (G'^2 + G''^2)^{1/2}$].

Eliminating the relaxation time also eliminates the effect of temperature (through its effect on relaxation time). However, temperature may have an influence on modulus.³² For the majority of polymer melts the time-temperature superposition applies³² and the temperature has a negligible effect on modulus. For the special case where the modulus shows a significant temperature dependence (such as in LDPE), all the polydispersity measures need to be redefined, as shown later.

The following measures of polydispersity have been used internally at Quantum for some time and satisfy the requirements outlined above.

Polydispersity at the High MW End

The following polydispersity measure, called ER , is extracted from G' vs. G'' data:

Table III Comparison of Polydispersity Index Values for Linear Polyolefins with Long Chain Branching

Polymer	PI	Mod Sep	ER	ET	RDR ^a	PDR
Virgin HDPE	2.4	2.4	4.2	15.6	5.1	26.9
3rd Pass through Extruder	2.6	2.3	4.6	20.4	6.4	32.0
5th Pass through Extruder	2.7	2.1	5.1	28.7	7.1	35.1
Virgin HDPE	4.7	2.0	5.0	45.5	11.6	53
75 ppm Peroxide Added	8.1	1.5	6.0	507	22.5	100
125 ppm Peroxide Added	12.2	1.3	6.5	1930	31.7	145
175 ppm Peroxide Added	21.7	1.1	6.7	10,000	48.9	253

^a AB = 0.72, A = 4, s = 1.0.

$$ER = C_1 \cdot G' |_{at G''_{ref}} \quad (19)$$

where G''_{ref} is selected to be a low modulus value (corresponding to low frequencies) and C_1 is a normalization constant. For polyolefin melts, good results have been obtained with $G''_{ref} = 5000 \text{ dyn/cm}^2$ and $C_1 = 1.781 \cdot 10^{-3}$. When the available data does not extend to G''_{ref} , use is made of the fact that a log-log plot of G' vs. G'' is very nearly linear in that region and extrapolation is possible (using the data at the two lowest decades of frequency).

The fundamental justification of ER is similar to that of the modified Cole-Cole plot; the value of G' at low G'' relates to the compliance [eq. (17)], which in turn, is a polydispersity measure [eq. (14)]. In fact, if G'' is within the terminal region [where eqs. (11) and (17) are valid], then:

$$ER = C_1 \cdot J_e^o \cdot (G''_{ref})^2 \quad (20)$$

In practice, for commercial broad polymer melts, the experimentally lowest accessible G''_{ref} is far from

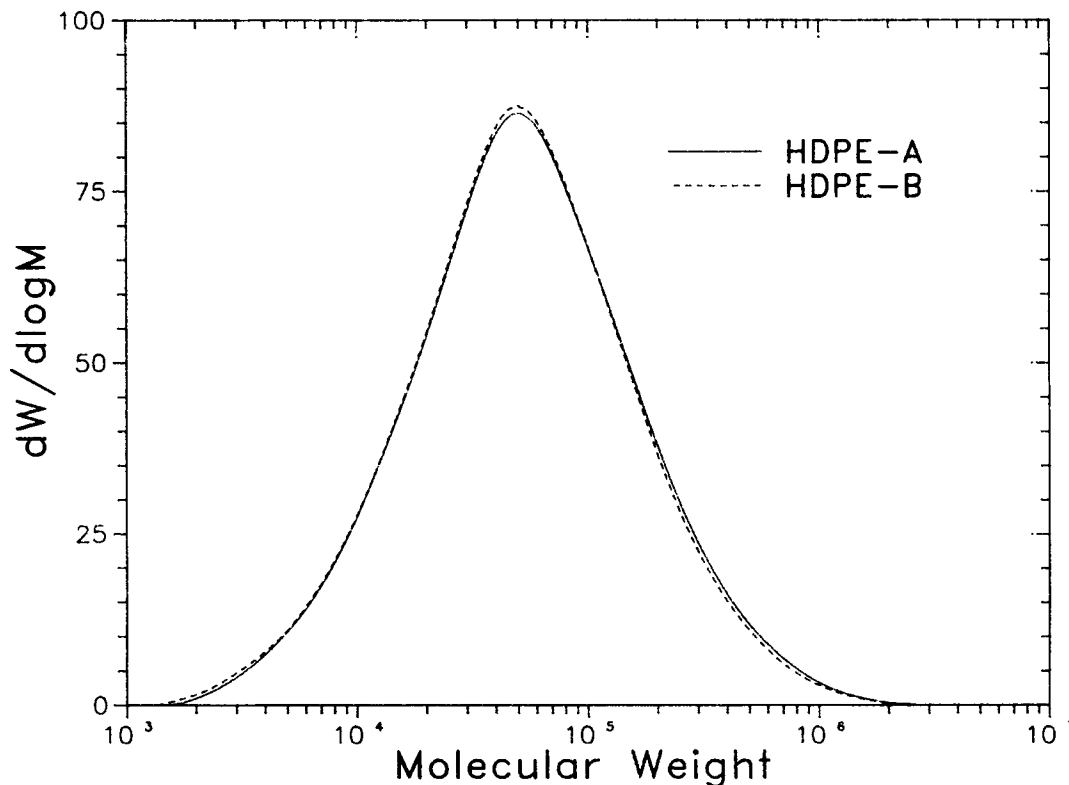


Figure 6 MWDs of two HDPE powders pelletized under different shearing conditions HDPE-A = severe, HDPE-B = mild.

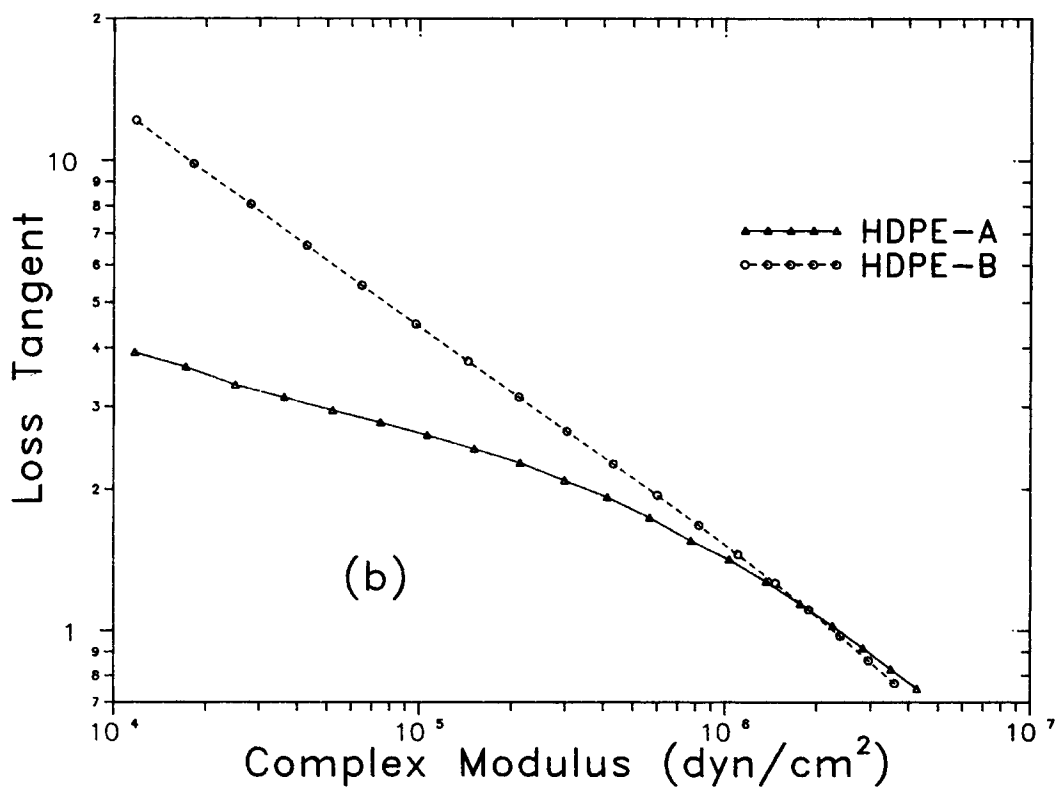
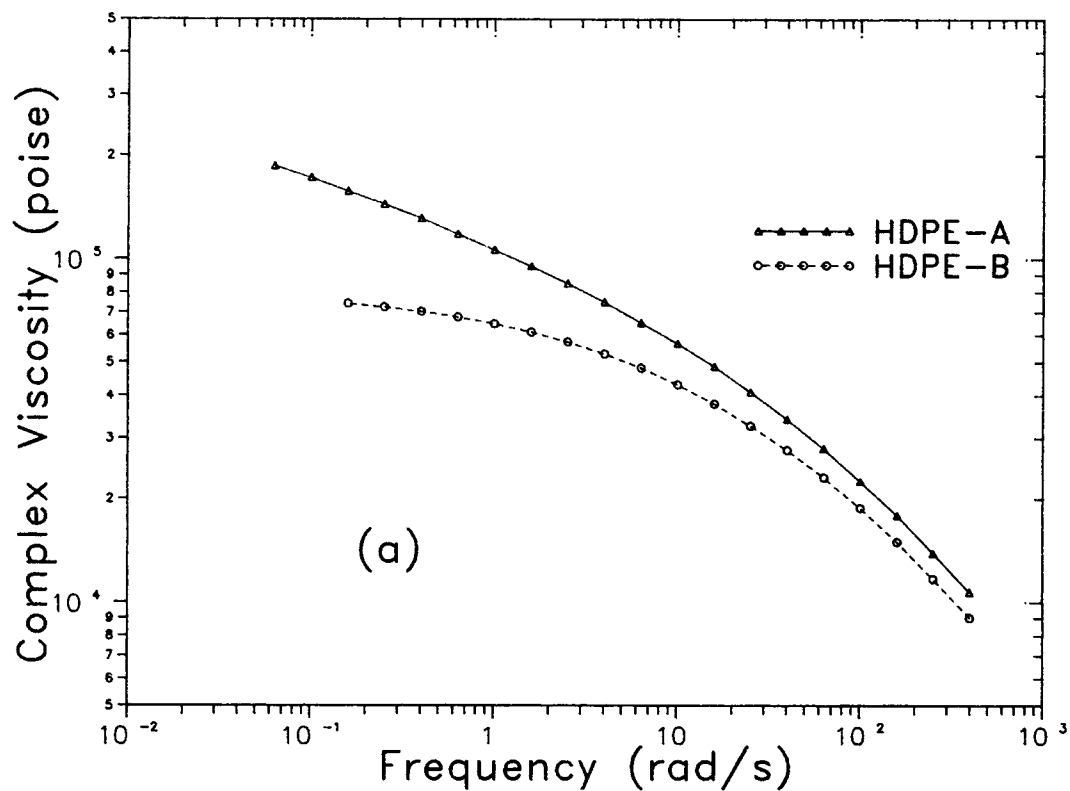


Figure 7 Linear viscoelastic data for the polymers of Figure 6. (a) Complex viscosity vs. frequency; (b) loss tangent vs. complex modulus.

Table IV Comparison of Two HDPEs of Nearly Identical MWDs and Different Levels of LCB

Polymer	PI	Mod Sep	ER	ET	RDR ^a	PDR
HDPE-A	0.61	4.2	2.0	1.1	1.9	4.8
HDPE-B	0.63	6.4	0.5	0.88	1.1	2.7

^a AB = 0.72, A = 2, s = 1.0.

the terminal region, as can be ascertained from the slope of the log G' vs. log G'' being much less than 2 (typically 1.0–1.5).

Note also that the ER measure is specifically designed to quantify high MW (or long time end) polydispersity. ER contains no contributions from the low MW end.

High Sensitivity High MW-End Polydispersity

For very high molecular weight polymers and/or extremely broad MWD, the G''_{ref} is so far from the terminal region that the discriminating power of ER diminishes to some extent. For those cases, a second polydispersity measure was designed. This measure is called ET and is derived from loss tangent vs. complex modulus data:

$$ET = \frac{C_2}{G^*} \Big|_{\tan \delta = C_3} \quad (21)$$

Typical values for the constants are $C_2 = 10^6 \text{ dyn/cm}^2$ and $C_3 = 1.5$. The justification of ET is similar to that of ER . Analytical results can be derived in the terminal region ($\omega \rightarrow 0, \tan \delta \gg 1$) where:

$$\tan \delta \equiv \frac{G''}{G'} \approx \frac{G''}{J_e^o \cdot (G'')^2} = \frac{1}{J_e^o \cdot G''} \quad (22)$$

The complex modulus is also related to G'' through:

$$G^* = \frac{G''}{\sin \delta} \quad (23)$$

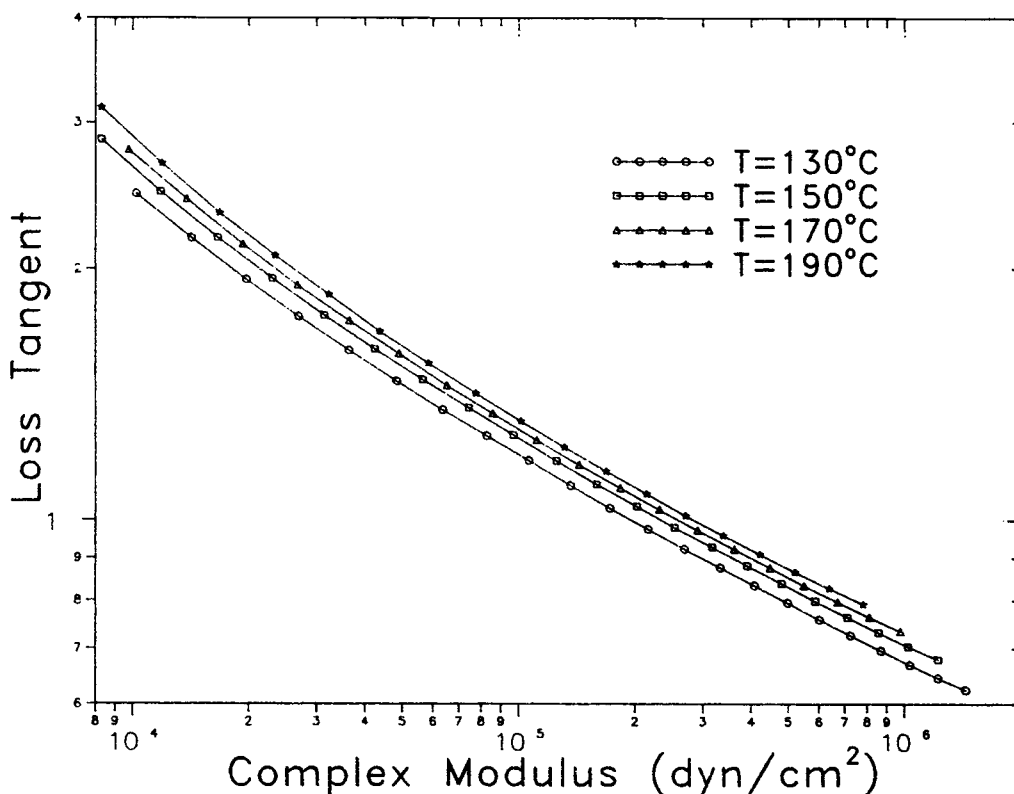


Figure 8 Loss tangent vs. complex modulus data at different temperatures for an LDPE (LDPE-4 in ref. 32) fall onto parallel curves due to the temperature dependence of modulus.

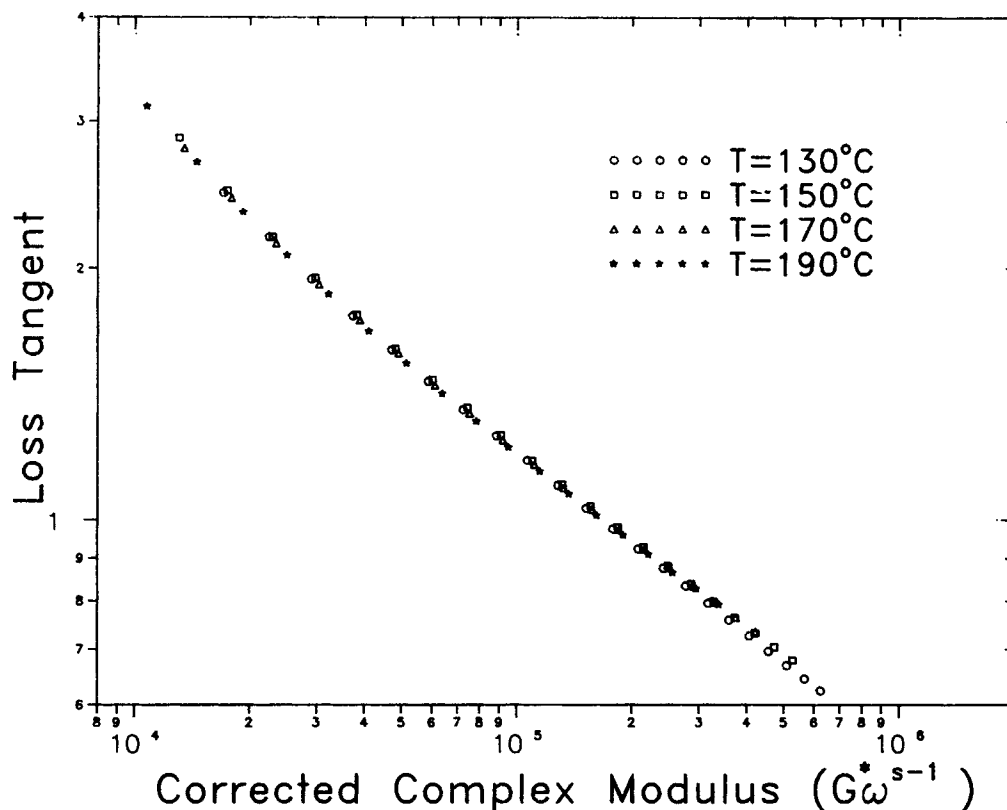


Figure 9 The data of Figure 8 superimpose after the correction of eq. (46) is applied.

Combination of eqs. (21) to (23) yields:

$$ET = C_2 \cdot J_e^0 \cdot \sin \delta \tan \delta \Big|_{\text{at } \tan \delta = C_3} \quad (24)$$

Therefore, in the terminal region, ET is also proportional to the compliance J_e^0 , just as ER .

Comparison of eq. (21) and eq. (6) shows that the PI measure derived from the crossover modulus is a partial case of ET for $C_3 = \tan \delta = 1$ and $C_2 = \sqrt{2} \cdot 10^6$. The advantage of ET is that one can use a high enough C_3 value so as to correspond to low modulus values and, thus, characterize high MW-end polydispersity.

Overall Polydispersity Measure, RDR

Both ER and ET characterize polydispersity at the high end. For situations when one is interested in an overall polydispersity, i.e., both the high and low MW contributions, the following measure is used.

$$RDR = \frac{C_4}{\eta_0 \omega_0^s} \quad (25)$$

where $C_4 = 4.1 \cdot 10^6 \text{ dyn/cm}^2$. The parameters η_0 , ω_0 are determined by fitting the Sabia equation²¹ to

the complex viscosity (η^*) vs. frequency (ω) data, in direct analogy to the R_D index [eqs. (2) and (3)]:

$$\ln\left(\frac{\eta^*}{\eta_0}\right) = \left(\frac{\eta^*}{\eta_0} - A\right) \cdot \ln\left[1 + \left(\frac{\omega}{\omega_0}\right)^B\right] \quad (26)$$

In practice, the ratio AB is fixed (0.72 for polyolefins) and the A -value is specified. Comparison of RDR numbers derived on the basis of different A -values is not meaningful. In order to compare the overall polydispersity for two or more polymer melts, the RDR numbers must be computed on the basis of the same A -value. However, very different polymers will not fit well with the same A -value. Therefore, RDR carries the restrictions of the Sabia equation fit, and is limited to cases of comparing similar polymers (of similar overall polydispersities).

Some comment is necessary here regarding the DRI measure [eq. (9)] that was recently proposed.³¹ The DRI measure in eq. (9) is derived from the three-parameter Cross viscosity model [eq. (8)] and, therefore, it is a partial case of the RDR measure above [with a fixed A -value in the Sabia equation, eq. (26), and the AB parameter corresponding to the power-law index n of the Cross model in eq.

Table V Polydispersity Measures Derived from Rheological Data on an LDPE without and with the Temperature Correction Applied

T, °C	PI	Mod Sep	ER	ET	RDR	PDR
Uncorrected data						
130	7.3	2.6	3.0	23.0	17.3 ^a	8.0
150	6.2	2.7	2.7	19.8	14.5 ^a	7.0
170	5.5	2.8	2.6	17.8	13.2 ^a	6.5
190	5.0	2.9	2.5	16.1	12.4 ^a	6.2
Corrected data						
130	8.6	3.3	2.2	18.3	14.2 ^b	28.9
150	8.3	3.5	2.1	17.8	13.7 ^b	28.5
170	8.4	3.5	2.1	18.2	14.0 ^b	29.4
190	8.5	3.6	2.1	18.5	14.5 ^b	31.1

^a AB = 0.72, A = 2.5, s = 1.

^b AB = 0.72, A = 2.5, s = 0.86.

(8)]. Consequently, the *DRI* will not be included in subsequent evaluations of the various polydispersity measures, but it should be remembered that the *DRI* has significance similar to the *RDR* with the additional limitation of a fixed *A*-value (and, thus, limited ability to fit a diverse range of viscosity curves).

Overall Polydispersity Measure, *PDR*

To circumvent the limitations of the *RDR* index, the *PDR* index was introduced. The *PDR* also uses complex viscosity (η^*) data, but as a function of complex modulus (G^*) rather than frequency. The complex viscosities η_1^* , η_2^* , η_3^* are calculated at three complex modulus values, $G_{\text{ref},1}^*$, $G_{\text{ref},2}^*$ = $(G_{\text{ref},1}^* \cdot G_{\text{ref},3}^*)^{1/2}$ and $G_{\text{ref},3}^*$ (by extrapolation or interpolation). The *PDR* index is then defined as:

$$PDR = \frac{\eta_1^*}{\eta_3^*} \cdot \frac{(\eta_1^* \cdot \eta_3^*)^{1/2}}{\eta_2^*} \quad (27)$$

The first term in eq. (27) is a measure of shear sensitivity. The second term in eq. (27) is a measure of curvature of the viscosity curve, with a larger curvature corresponding to smaller polydispersity. The reference modulus values are typically selected as $G_{\text{ref},1}^* = 1.95 \cdot 10^4$ dyn/cm² and $\log_{10}(G_{\text{ref},3}^*/G_{\text{ref},1}^*) = 2$ for linear polyolefins, whereas $G_{\text{ref},1}^* = 10^4$ dyn/cm² and $\log_{10}(G_{\text{ref},3}^*/G_{\text{ref},1}^*) = 1.5$ for long chain branched polyolefins. These values are selected so that they cover as wide a range as possible and, at the same time, so that they are accessible experimentally for the majority of materials of interest.

EVALUATION OF POLYDISPERSITY MEASURES USING MODEL SPECTRA

The previously described polydispersity measures will now be evaluated using some model relaxation spectra. The choice of model spectra allows an evaluation of the polydispersity measures that is particularly convenient; the spectra is exactly known and the characterization capability of the polydispersity measures can be unambiguously assessed. However, testing of the polydispersity measures with actual polymers will be given later.

As a first test case, the following model relaxation spectrum was selected:

$$H(\tau) = \frac{G_N^0}{\sigma(2\pi)^{1/2}} \cdot \exp \left[-\frac{\log_{10}^2 \left(\frac{\tau}{\tau_m} \right)}{2\sigma^2} \right] \quad (28)$$

$$\sigma = \frac{1}{\ln(10)} \cdot \left[\ln \left(\frac{\tau_w}{\tau_n} \right) \right]^{1/2}$$

$$\tau_m = (\tau_n \cdot \tau_w)^{1/2}$$

$$\tau_n = \frac{\eta_0}{G_N^0} \quad (29)$$

The parameters of the model spectrum are the zero shear viscosity (η_0), the plateau modulus (G_N^0) and the relaxation spectrum polydispersity. Because the spectrum is a log-normal distribution, the polydispersity is uniquely characterized by the τ_w/τ_n ratio.

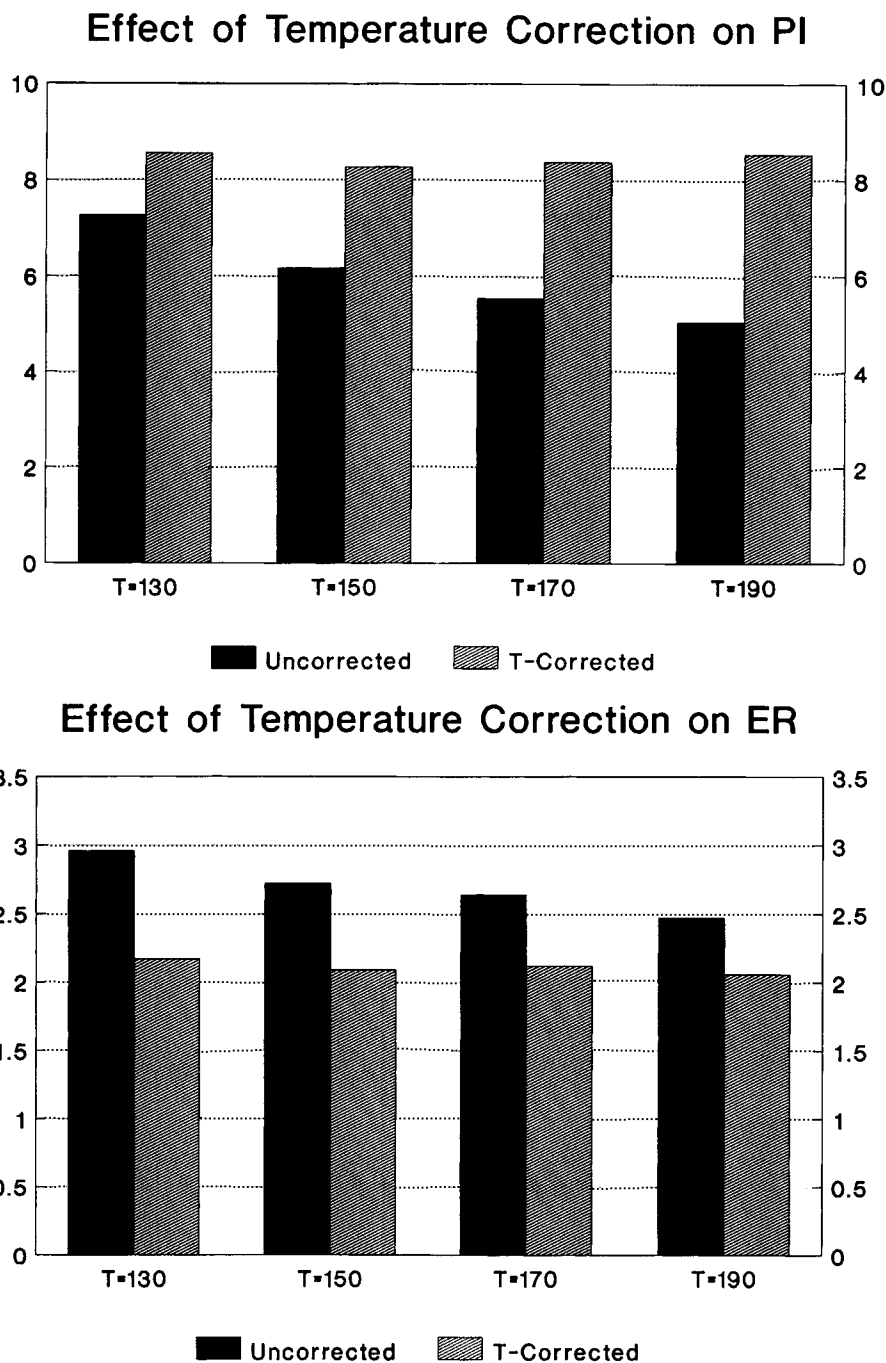


Figure 10 Effect of temperature correction on polydispersity measures derived from the data of Figures 8 and 9. (a) Effect on PI ; (b) effect on ER .

For the numerical calculations, the plateau modulus was fixed at $2 \cdot 10^7$ dyn/cm² (a polyethylene-like polymer), the zero-shear viscosity was fixed at $5 \cdot 10^5$ poise, and the ratio τ_w/τ_n was varied in the range 10^3 – 10^4 . Graphical results for the model spectra are shown in Figure 1. Note that the normalized, weighted relaxation spectrum, $\tau \cdot H(\tau)/\eta_0$,

is plotted on the y-axis so that the area under all curves is the same (for the purposes of comparison). Note also that in this representation the y-ordinate at a given relaxation time represents the contribution of that given relaxation time to zero-shear viscosity. It can be readily observed that, as the ratio τ_w/τ_n increases, the spectrum becomes broader. The

corresponding frequency response data are shown in Figure 2(a) over the range 10^{-2} – 10^3 rad/s (this range is the experimentally accessible range in practice). Replotting these data in the form of storage modulus (G') vs. loss modulus (G'') in Figure 2(b) immediately shows the differences; at a given level of G'' , the broader the spectrum (higher τ_w/τ_n), the higher the G' .

Another representation of these data in a form that is even more sensitive to differences in polydispersity is given in Figure 2(c), where the loss tangent is plotted against complex modulus. For the broader spectrum, the results show a lower loss tangent at a given complex modulus, especially at lower levels of complex modulus. Note that in both Figure 2(b) and (c) the curves converge at high modulus values and, therefore, for best discrimination sensitivity one needs to go to lower modulus values.

One point that needs clarification is the variables plotted in Figure 2(c). Both the loss tangent and the complex modulus are derived from G' and G'' :

$$\tan \delta = \frac{G''}{G'}$$

$$G^* = [(G')^2 + (G'')^2]^{1/2} \quad (30)$$

Therefore, it might appear that one is plotting the same variables on both axes of Figure 2(c), which is to be avoided.³³ However, note that the loss tangent and the complex modulus are the independent variables and the ones that are actually measured experimentally (the phase angle for the loss tangent and the torque for the complex modulus). Therefore, plotting the data in the form of Figure 2(c) is actually recommended on statistical grounds.³³

The various polydispersity measures were calculated from the data of Figure 2 and are plotted against the spectral breadth in Figure 3. Note that the spectral breadth (τ_w/τ_n) changes by a factor of 10, but the largest increase in the rheological polydispersity measures is less than 2. This is due to the fact that the terminal region, where the various polydispersity measures would be proportional to τ_w/τ_n , is inaccessible experimentally. Therefore, one is forced to extract a polydispersity measure from data over the experimentally available range and, thus, sacrifice sensitivity.

Inspection of Figure 3 shows the expected trend; all polydispersity measures increase monotonically as the relaxation spectrum broadens (higher τ_w/τ_n). Note also that all the curves are concave downward, i.e., the sensitivity diminishes at higher τ_w/τ_n . The

diminishing sensitivity means that it becomes increasingly difficult to differentiate spectral breadth as the spectrum broadens more and more. From Figure 3 we also see that the Modulus Separation (ModSep) is the least sensitive, followed by the *PI* index (based on the crossover modulus). All four polydispersity measures proposed in the present work perform better, with *ER* and *ET* performing the best.

The above test of the sensitivity of the various polydispersity measures leaves one question unanswered; namely, the discriminating power of the polydispersity measures for nonsymmetric spectra. Note that the model spectra of Figure 1 are log-normal distributions, which are symmetric around the mean, and the various averages are related through:

$$\frac{\tau_n}{\tau_H} = \frac{\tau_w}{\tau_n} = \frac{\tau_z}{\tau_w} \quad (31)$$

where τ_H , τ_n , τ_w , τ_z are the harmonic-, number-, weight- and z-average relaxation times, respectively.

To test the sensitivity of the various polydispersity measures with respect to the low and high sides of the relaxation spectrum, the following comparison was made. Model relaxation spectra were composed by blending two log-normal distributions so that the moment ratios τ_n/τ_H and τ_w/τ_n could be changed independently. Four relaxation spectra were derived in this fashion. All four have the same plateau modulus (G_N^0) and zero-shear viscosity (η_0). The moment ratios of the four spectra are given in Table I. Note that those spectra having $\tau_n/\tau_H = \tau_w/\tau_n$ are still nonsymmetric due to their being a blend of two log-normal distributions (bimodal). The four spectra are shown graphically in Figure 4. Note that at the long time end ($\tau > 10$ s) spectra *A* and *B* overlap and are narrow, whereas *C* and *D* overlap and are broader. At the short time end ($\tau < 0.01$ s) it is *A* and *C* that overlap and are narrow, whereas *B* and *D* overlap and are broader. Therefore, if we wanted to characterize the polydispersity of these spectra, we would need to be careful to identify from where the polydispersity is coming, either the long or the short time end. Visually, from Figure 4 and from the ratios of Table I we would classify the polydispersity of the spectra as:

$$\begin{aligned} \text{Long Time End: } A = B, \text{ Narrow } (\tau_w/\tau_n = 10^3) \\ C = D, \text{ Broad } (\tau_w/\tau_n = 10^4) \\ \text{Short Time End: } A = C, \text{ Narrow } (\tau_n/\tau_H = 10^3) \\ B = D, \text{ Broad } (\tau_n/\tau_H = 10^4) \end{aligned}$$

The above pairing of the spectra becomes evident from the frequency response data in Figure 5(a). Data for *A,B* and *C,D* overlap at low frequencies (corresponding to the long time end), and data for *A,C* and *B,D* overlap at high frequencies (corresponding to the short time end). The differences in polydispersity are more apparent in Figure 5(b,c). It is of interest to comment on polydispersity using the most sensitive representation, that of loss tangent vs. complex modulus in Figure 5(c) in combination with the various polydispersity measures calculated from the data of Figure 5 and listed in Table I.

Clearly, the *ER* measure characterizes best the polydispersity at the long time end, because $ER = 0.82$ for *A,B* and $ER = 1.6$ for *C,D*, faithfully reflecting the trend observed visually in Figure 5(c) (*A,B* data overlap at low complex modulus values and are at higher loss tangent than data for *C,D*).

The situation is more complex for polydispersity measures that include contributions from the short time end (*PI*, *RDR*, *PDR*). Specifically, *PI* would give a false picture of polydispersity because it would classify the four spectra as:

$$B > D > A > C$$

This order is obviously incorrect by reference to the full data set in Figure 5(c) and Table I. Note that in Figure 5(c) we would expect *A,C* to overlap at high complex modulus and *B,D* to also overlap and be broader (at lower loss tangent than *A,C*). This picture actually does emerge, but at much higher complex modulus values (corresponding to frequency values 10^3 – 10^5 , which are inaccessible experimentally), as shown in the inset in Figure 5(c).

The best delineation of the polydispersity of the spectra is provided by a combination of two polydispersity measures proposed in the present work. For example, spectra *B,C* have similar *PDR* (overall polydispersity), but spectrum *B* has lower *ER* (narrower at the long time end). Therefore, spectrum *B* must be broader at the short time end, as, indeed, is the case (τ_n/τ_H is 10^4 for *B* compared to 10^3 for *C*). Similarly, *C* and *D* have same *ER* (similar breadth at the long time end), but *D* has higher *PDR* (greater overall polydispersity). Therefore, *D* must be broader at the short time end, as, indeed, shown by the τ_n/τ_H ratio (10^4 for *D* vs. 10^3 for *C*).

The above test indicates that for nonsymmetric distributions the literature measures of polydispersity fail. Specifically, the *PI* measure derived from the crossover modulus contains significant contri-

butions from the short time end of the spectrum and is not an appropriate polydispersity measure for nonsymmetric distributions. The presently proposed polydispersity measures can differentiate polydispersity at the long time end, particularly the *ER* measure. Overall polydispersity measures, such as *RDR* and *PDR*, can be used in combination with *ER* to characterize indirectly polydispersity at the short time end. There is still a need for a polydispersity measure characterizing the short time end free from contributions from the long time end.

EVALUATION OF POLYDISPERSITY MEASURES ON POLYMER MELTS

Further evaluation of the various polydispersity measures has been performed with numerous polymeric materials. Some representative data are given below. The polydispersity measures were evaluated from the rheological data on linear polyolefins whose molecular weight information was given in our previous publication (Table I in ref. 11).

Results are listed in Table II. The first group is a series of blends of two HDPEs of very different molecular weight. All polydispersity measures, except the Modulus Separation, show the polydispersity to go through a maximum as a function of HMW fraction, a feature that is well established in binary blends of different molecular weight materials.^{34,35} The Modulus Separation fails to characterize polydispersity.

Similar results were observed with a series of three commercial, broad HDPEs (HDPE-1,2,3) and four narrow LLDPEs (LLDPE-1,2,3,4).

As was mentioned earlier and emphasized in our previous publication,¹¹ rheological polydispersity may come from two sources: molecular weight distribution (MWD) and long chain branching (LCB). In the case of HDPE, increasing LCB results in increasing rheological polydispersity. Two examples were given in ref. 11, the first a HDPE that was put through successive extrusion passes, and the second a HDPE with increasing levels of a peroxide added. It was shown in ref. 11 that the MWDs in both cases remain virtually unchanged, but the rheological properties change significantly. The polydispersity measures are listed in Table III. Again, except for the Modulus Separation, all polydispersity measures show an increasing trend with increasing number of extrusion passes or increasing peroxide content (i.e., increasing level of LCB).

From the results of Tables II and III, we see the *PI* polydispersity measure (derived from the cross-

over modulus) does characterize polydispersity, perhaps at reduced sensitivity compared to the polydispersity measures of the present work. The advantage of using the crossover modulus is that determination of the crossover modulus does not require data at low frequencies. Therefore, the time required for data collection can be very short, which opens possibilities for online monitoring of polymer reactors and fast feedback control. However, it should be emphasized that low frequency data are necessary for unambiguous characterization of long time end polydispersity. This fundamental fact was demonstrated with the model spectra in the previous section and will be illustrated below with an actual example from industrial practice.

A HDPE was produced in powder form and the powder was pelletized in two different extruders under very different conditions. HDPE-A was pelletized under severe shear conditions, whereas HDPE-B was pelletized under relatively mild shear conditions. One would expect the MWD to be nearly the same, but the LCB content to be very different. That the MWDs are nearly identical was confirmed by Gel Permeation Chromatography, as shown in Figure 6. Rheological data on these two polymers show distinct differences, as illustrated in Figure 7(a). However, the *PI* measure in Table IV shows these two materials to be practically the same, in contrast to all other polydispersity measures. The reason is shown in Figure 7(b), where the loss tangent is plotted against complex modulus. Note that the two curves converge and crossover around $\tan \delta = 1$, which is the reason for the same *PI* value. However, the differences at low modulus values are obvious. If polydispersity for these two materials were characterized with *PI*, one would have missed the difference. Therefore, the conclusion is that one needs to obtain rheological data at the lowest modulus levels (or frequencies) possible in order to probe polydispersity at the long time end.

From Table IV one can also observe that the *ET* measure shows a smaller difference than the *ER* measure between HDPE-A and HDPE-B. This is due to the fact that *ET* was evaluated at $\tan \delta = 1.5$ [eq. (21)], which for these two HDPEs falls at rather high modulus values. In this case, the *ET* does not satisfy its intended purpose of characterizing long time-end polydispersity, and should be redefined at a higher $\tan \delta$ value. As a rule of thumb, *ET* values around unity are at too high modulus values ($\sim 10^6$ dyn/cm²) and should be redefined at a higher loss tangent level.

THE EFFECT OF TEMPERATURE ON POLYDISPERSITY MEASURES

The effect of temperature on polyolefin melt rheology was considered by the present authors in ref. 32. It was shown that for most polyolefins the modulus is practically temperature independent. For these polyolefins and all other polymer melts obeying time-temperature superposition,³² the polydispersity measures considered in this work will be temperature independent. When the modulus shows appreciable temperature dependence, as is the case for long chain branched polyethylenes (notably LDPE), the polydispersity measures will show an undesirable temperature dependence. For those materials, the polydispersity measures need to be suitably redefined, as shown below.

For the general case when both the modulus and relaxation time show a temperature dependence, it was shown in ref. 32 that the following describes the temperature dependence of the relaxation spectrum:

$$b_T H(\tau/\alpha_T, T) = H(\tau, T_o) \quad (32)$$

where α_T and b_T are the "horizontal" and "vertical" shift factors respectively, T is the temperature and T_o is a reference temperature. The horizontal shift factor α_T reflects essentially the temperature dependence of relaxation time:

$$\tau(T) = \tau(T_o) \cdot \alpha_T \quad (33)$$

while the vertical shift factor b_T reflects the temperature dependence of modulus

$$G_N^o(T) = G_N^o(T_o)/b_T \quad (34)$$

The temperature shift factors are expressed in terms of a "horizontal" (E_H) and a "vertical" (E_V) activation energy:

$$\alpha_T = \exp \left[\frac{E_H}{R} \left(\frac{1}{T + 273} - \frac{1}{T_o + 273} \right) \right] \quad (35)$$

$$b_T = \exp \left[\frac{E_V}{R} \left(\frac{1}{T + 273} - \frac{1}{T_o + 273} \right) \right] \quad (36)$$

It can be shown that the temperature dependence of frequency response data in the linear viscoelastic region is given by:

$$\begin{aligned} b_T G'(\alpha_T \omega, T) &= G'(\omega, T_o) \\ b_T G''(\alpha_T \omega, T) &= G''(\omega, T_o) \end{aligned} \quad (37)$$

From the above, we see that the loss tangent shifts as:

$$\tan \delta(\alpha_T \omega, T) = \tan \delta(\omega, T_o) \quad (38)$$

i.e., the loss tangent remains invariant under a temperature shift. Therefore, it is convenient to redefine the various viscoelastic properties in terms of the loss tangent and temperature:

$$G'(T, \tan \delta) = \frac{1}{b_T} G'(T_o, \tan \delta)$$

$$G''(T, \tan \delta) = \frac{1}{b_T} G''(T_o, \tan \delta)$$

$$\omega(T, \tan \delta) = \frac{1}{\alpha_T} \omega(T_o, \tan \delta) \quad (39)$$

$$G^*(T, \tan \delta) = \frac{1}{b_T} G^*(T_o, \tan \delta) \quad (40)$$

$$\eta^*(T, \tan \delta) = \frac{\alpha_T}{b_T} \eta^*(T_o, \tan \delta) \quad (41)$$

It can be shown from the above that the compliance is also temperature dependent:

$$\frac{J_e^o(T)}{J_e^o(T_o)} = b_T \quad (42)$$

Because most polydispersity measures were shown to relate to the compliance, it follows that all the polydispersity measures will have a temperature dependence associated with the "vertical" shift factor, b_T , i.e., with the temperature dependence of modulus. For example, the *PI* measure derived from the crossover modulus will have the following temperature dependence:

$$\frac{PI(T)}{PI(T_o)} = b_T \quad (43)$$

whereas *ER* will have the following temperature dependence:

$$\frac{ER(T)}{ER(T_o)} = b_T^m$$

$$m = \frac{d \log G'}{d \log G''} - 1 \quad (44)$$

Because the exponent m is generally less than unity (m is 0.3–0.5 for commercial broad polyole-

fins), the temperature sensitivity of *ER* will be less than that of *PI*. However, in both cases the magnitude of the temperature effect depends on the "vertical" activation energy [E_V in eq. (36)]. For $E_V = 0$ then $b_T = 1$, and there is no temperature dependence. For a typical LDPE, E_V is around 2 kcal/gmol.³² Then for $T = 130^\circ\text{C}$ and $T_o = 190^\circ\text{C}$, we have $b_T = 1.38$, and, therefore, the *PI* derived from the 130°C data will be 38% higher than that derived from the 190°C data. Clearly, this is unacceptable, and some remedy is necessary.

There are two ways to accommodate cases of temperature-dependent modulus:

1. Shift the data at a reference temperature [eq. (39)] and derive a polydispersity measure from the data at the reference temperature. This requires both the horizontal and vertical activation energies (E_H , E_V).
2. Redefine the polydispersity measures to normalize out the effect of temperature. This requires a parameter s , which relates to the activation energies through:

$$s = 1 - \frac{E_V}{E_H} \quad (45)$$

The first option above is straightforward and will not be pursued further. Note, however, that it requires both E_H and E_V . It turns out that at least for LDPE the parameter s in eq. (45) changes little, although E_H and E_V vary somewhat. Therefore, it is worth pursuing the second option (which requires only the ratio of E_H , E_V).

From eq. (39) it can be shown that:

$$G^*(T, \tan \delta) \cdot [\omega(T, \tan \delta)]^{s-1}$$

$$= G^*(T_o, \tan \delta) \cdot [\omega(T_o, \tan \delta)]^{s-1} \quad (46)$$

i.e., multiplying modulus by frequency raised to the $(s-1)$ power removes the vertical shift factor. This is illustrated with actual data on an LDPE in Figure 8 and 9. Data on an LDPE (LDPE-4 from ref. 32) are shown in Figure 8 in the form of loss tangent vs. complex modulus at different temperatures. It can readily be observed that the data fall onto parallel curves, which is due to the temperature dependence of modulus.³² To apply the correction of eq. (46), each data point in Figure 8 is multiplied by the corresponding frequency raised to the $(s-1)$ power, where $s = 1 - 2.28/16.01 = 0.86$ (Table 5 in ref. 32). The result is illustrated in Figure 9: now

the data from all four temperatures superimpose adequately, and polydispersity measures derived from these corrected data will be temperature independent.

To apply the correction of eq. (46) to actual data, the procedure is straightforward. All moduli at a given temperature are multiplied by ω^{s-1} and the polydispersity measures are derived from the modified data. For example, the modified *ER* is now derived from $(G'\omega^{s-1})$ vs. $(G''\omega^{s-1})$ data. For *RDR*, one can still fit the Sabia equation to the uncorrected data and apply the correction to the calculation of *RDR* [parameter *s* in eq. (25)].

The application of the temperature correction to the polydispersity measures is given in Table V and illustrated in Figure 10 for the data on the LDPE considered earlier. For example, the *PI* measure when uncorrected is shown to decrease significantly with temperature in Figure 10(a), but remain practically constant after the temperature correction is applied. Similarly, the *ER* measure derived from uncorrected data shows a decreasing trend with temperature in Figure 10(b), and this temperature dependence is removed when the correction is applied.

CONCLUDING REMARKS

The approaches proposed in the literature for extracting a polydispersity measure from rheological data were reviewed. The requirements for an effective polydispersity measure were identified. New polydispersity measures were proposed that adequately satisfy most requirements.

Both the literature and the new polydispersity measures were analyzed on fundamental grounds. It was shown that when the rheological data are in the terminal region most polydispersity measures relate to the steady-state compliance, J_e^0 , which in itself is proportional to the polydispersity of the relaxation spectrum [eq. (14)]. The exception is the *PI* measure [eq. (6)] derived from the crossover modulus and which, by definition, is always outside the terminal region. However, in actual practice, the rheological data almost never extend into the terminal region and the various polydispersity measures must be derived from the experimentally accessible data.

It was shown with model calculations that for a symmetric relaxation spectrum, as the spectrum broadens, all polydispersity measures increase, albeit with different degrees of sensitivity. The polydispersity measures of the present work all display bet-

ter sensitivity. Model calculations with nonsymmetric spectra show that the *PI* measure contains significant contributions from the short time end. The only effective way to characterize polydispersity in these nonsymmetric spectra is by combination of two of the proposed measures of this work (one for polydispersity at the long time end, such as *ER*, and one for overall polydispersity, such as *RDR* or *PDR*). The performance of the various polydispersity measures was also illustrated with examples from industrial practice.

The presence of small levels of long chain branching in an otherwise linear polymer alters most measures of polydispersity dramatically, while no detectable change appears in the molecular weight distribution obtained using a gel permeation chromatograph.

It was shown that for a temperature-dependent modulus, which is the case in long chain branched polyethylene (e.g., LDPE), the polydispersity measures display an undesirable dependence on temperature, decreasing with increasing temperature. Appropriate procedures to eliminate the effect of temperature were described and illustrated with an example on LDPE.

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Received November 11, 1994

Accepted February 25, 1995