

# DETERMINING MOLECULAR WEIGHT DISTRIBUTIONS FROM THE RHEOLOGICAL PROPERTIES OF POLYMER MELTS

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This note is a summary of the state-of-the-art for determining molecular weight distributions from melt rheological properties. It consists of a short introduction, including a summary of the models used, and then focuses on the so-called "Modulus Model" with emphasis on an evaluation of the recently commercialized software from Rheometric Scientific, Inc. It will conclude with a short look into the future. My apologies to all the contributors to the literature who have not been mentioned due to the limited scope of this paper.

## Acknowledgements

I gratefully acknowledge the careful, well thought out work of Dr. Patricia Cotts of the DuPont Company. She is one of my chief collaborators in this research supplying high quality size exclusion chromatography (SEC) data using multi-angle light scattering, refractive index and viscosity detection. Mark Grehlinger (Rheometric) was invaluable for writing the MWD determination software and modifying it in a timely fashion. He is a pleasure to work with: prompt, cooperative and highly competent. Prof. Dave Mead (U. Michigan) was the main driving force for developing and commercializing the Rheometric technique for MWD determination.

## Introduction

Although the recent literature abounds with examples of determining the MWD from rheological properties, many people still wonder why one would bother when SEC has been around for decades and is the classical technique for such determinations. One answer is that SEC requires dissolution of the sample and some polymers are difficult to dissolve, like the semicrystalline fluoropolymers made from tetrafluoroethylene.<sup>1-3</sup> However, even for polymers which can be dissolved reasonably easily, rheological measurements are capable of detecting subtle structural differences between samples that SEC is not capable of, such as long chain branching (LCB).<sup>4</sup> I do not want to leave the impression that SEC and rheology are competing techniques. Quite the contrary, they complement each other nicely, for example, in determining the probable presence of LCB. Both techniques therefore work together in defining

structures needed to get desired rheological behavior and leading to more precise characterization for patent protection.

### Methods of Determining MWD from Rheology

Two general models have been used for MWD determinations: the “Viscosity Model” and the “Modulus Model”. The first workable method of determining MWD from the “Viscosity Model”<sup>5,6</sup> was based on the work of Bersted and Slee<sup>7</sup> as well as Malkin and Teishev.<sup>8</sup> The model is derived from some simple assumptions relating molecular structure to the viscosity flow curve. First, the zero shear viscosity ( $\eta_0$ ) of a polydisperse mixture is assumed to be proportional to the 3.4 power of the weight average molecular weight,  $\bar{M}_W$ .

$$\eta_{0,mix} = K_1(\bar{M}_W)^{3.4} \quad (1)$$

Next, the deformation rate,  $r$ , axis is transformed to molecular weight using Equation (2)

$$\frac{1}{r} = K_2(M)^{3.4} \quad (2)$$

where  $r$  can be either the shear rate ( $\dot{\gamma}$ ) in a steady shear flow experiment or the frequency ( $\omega$ ) in oscillatory flow. Finally, a very simplistic flow curve is assumed for each monodisperse component. The double logarithmic plot of the flow curve is assumed to be constant below a critical deformation rate ( $r_c$ ) and above this rate has a slope of “-1” as depicted in Equations (3) and (4).

$$\eta(\dot{\gamma}) \text{ or } \eta^*(\omega) = \text{constant} \quad [r < r_c] \quad (3)$$

$$\eta(\dot{\gamma}) \text{ or } \eta^*(\omega) = K_3 r^{-1} \quad [r > r_c] \quad (4)$$

In this paper, however, we will be stressing the “Modulus Model” because we think it is far more sensitive to low concentrations of high MW components which usually dominate melt processability. The latter is especially true when extensional flows are involved.<sup>9</sup> A generalized form of this model is represented in Equation (5), as presented by Meier, et. al.<sup>10</sup> in terms of the relaxation modulus,  $G(t)$ .

$$\frac{G(t)}{G_N^0} = \left( \int_{\ln(M_e)}^{\infty} F^{1/\beta} F(t,M) w(M) d(\ln M) \right)^\beta \quad (5)$$

In Equation (5)  $G(t)$  is normalized by the plateau modulus,  $G_N^0$ .  $F(t,M)$  is a kernel function describing the relaxation behavior of a monodisperse component of molecular weight  $M$ , where the time is related to  $M$  by Equation (6).

$$t = K_4 (M)^{3.4} \quad (6)$$

$w(M)$  is the weight fraction MWD function. The exponent,  $\beta$ , is a parameter which characterizes the mixing behavior of the chains. For example,  $\beta$  is 1 for simple reptation and 2 for double reptation theory.  $M_e$  is the entanglement MW.

The following “conventional” kernel functions,  $F(t,M)$ , have typically been used.<sup>10,11</sup>

- *The Step-Function* is the simplest function. It assumes that the monodisperse component with  $M$  molecular weight will relax instantly at a time  $t = \tau_o(M)$  as described in Equations (7). Although this is a somewhat

$$F_1(t,M) = 1 \text{ if } t < \tau_o(M) \quad (7a)$$

$$F_1(t,M) = 0 \text{ for all other } t \quad (7b)$$

unrealistic description of relaxation behavior, its simplicity enables one to determine the MWD without resorting to complex mathematical procedures like regularization.

- *The Single Exponential* is the simplest relaxation function approximating the relaxation behavior in a qualitatively realistic way.

$$F_2(t,M) = \exp[-t/\tau_o(M)] \quad (8)$$

- *The Doi Kernel* is a summation of single exponentials which describes a more gradual and more quantitatively realistic relaxation.

$$F_3(t,M) = \frac{8}{\pi^2} \sum_{n \in \text{odd}} \frac{\exp[-tn^2/\tau_o(M)]}{n^2} \quad (9)$$

- *The BSW Kernel*

$$F_4(t,M) = \alpha \int_0^1 u^{\alpha-1} \exp[-t/\tau_o(M)u] \quad (10)$$

where,

$$\alpha = \sqrt{\frac{J_e^0 G_N^0}{J_e^0 G_N^0 - 1} - 1}$$

- *The des Cloizeaux Kernel*

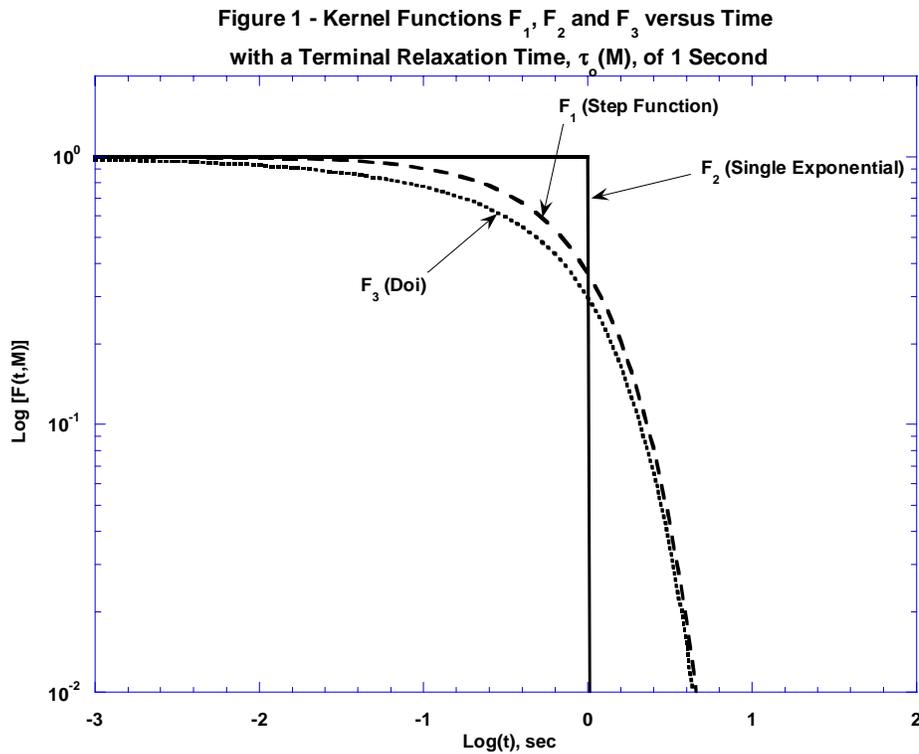
$$F_5 = \left( \frac{8}{\pi^2} \sum_{n \in \text{odd}} \frac{1}{n^2} \exp \left\{ -n^2 \left[ \frac{t}{\tau_0(M)} + \frac{M}{12.5M_e} g \left( \frac{tM}{12.5M_e \tau_0(M)} \right) \right] \right\} \right)^2 \quad (11)$$

where,

$$g(x) = \sum_{m=0}^{\infty} \frac{1 - \exp(-m^2 x)}{m^2}$$

and  $J_e^0$  is the steady state compliance.

The BSW and des Cloizeaux kernels are even more mathematically sophisticated than the Doi kernel and have even more flexibility in describing relaxation behavior. Figure 1 represents  $F_1$ ,  $F_2$  and  $F_3$  graphically. Functions  $F_4$  and  $F_5$  would be similar to  $F_3$ .



Some precautions are in order when dealing with these models. First, and very importantly, they apply only to polymers with no LCB. Other assumptions are that we are dealing with a polymer that: is unblended with either fillers or another polymer; has no ionic interactions; is completely melted with no remnants of crystallinity remaining. In short, we must deal with a polymer melt in which the entanglements overwhelmingly dominate the relaxation. Also, only very small amounts of oligomer less than the critical MW ( $M_c$ ) can be present. Substantial amounts of low MW material will dilute the polymer and give a falsely low reading in MW. Finally, we assume that we are dealing with random coil chains (i.e. not liquid crystalline systems).

### **An Historical Comparison of Modulus Models**

Wu<sup>12,13</sup> was one of the first to attempt MWD calculations from rheological data. He assumed single reptation and single exponential behavior governed the relaxation. Thus,  $\beta = 1$  and  $F_2$ , the Single Exponential kernel, were used in Equation (5). This led to an adequate representation of nearly monodisperse samples but very poor representation of bimodal blends.

Tuminello<sup>14</sup> assumed double reptation ( $\beta = 2$ ) and the oversimplifying Step Function behavior for the kernel [ $F(t,M) = F_1$ ]. Although these assumptions predicted a falsely broad distribution for nearly monodisperse melts, the predictions were reasonably accurate for bimodal blends and broad distribution polymers. A clear advantage in predicting the MWD of bimodal blends was illustrated in Fig. 20 of Reference 14 versus using the simple reptation assumption of Wu.

Mead<sup>15</sup> improved the representation of nearly monodisperse, broad and bimodal distribution melts as illustrated in Figure 7 of Reference 15. He used the double reptation assumption with a Single Exponential kernel ( $\beta = 2$ ;  $F(t,M) = F_2$ ). Mead's approach was commercialized by Rheometric Scientific and the remainder of this paper is devoted to its evaluation.

### **Evaluation of Rheometric Scientific Software**

The software is documented in the Rheometric Scientific literature.<sup>16,17,18</sup> Well-characterized polystyrenes were used in our evaluations. The software requires storage ( $G'$ ) and loss ( $G''$ ) modulus data as a function of frequency. We chose to ensure that we had a complete data set at low frequency because of our interest in the high MW components. In many cases, we were able to get well into the terminal zone through the use of creep/recoil data and transforming it to  $G'$ ,  $G''$  via the method described by Plazek, et. al.<sup>19</sup> We minimized the effects of transition zone overlap by deleting any data where  $G' > 0.8 G_N^0$ . An accurate value of  $G_N^0$  ( $1.70 \times 10^5$  Pa)<sup>14</sup> was needed for an accurate determination of the distribution breadth. The "Front Factor",  $K_4$  defined in Equation (6), had to be empirically determined, as a calibration step, for an

accurate estimation of the MW averages.  $K_4 = 4.52 \times 10^{-18}$  for the “Old Polystyrene Data” and  $3.02 \times 10^{-18}$  for the “New Data”. All data was shifted to 160°C prior to analysis.

The fitting of Equation (5) to the  $G'(\omega)$ ,  $G''(\omega)$  data is the most crucial part of the operation. It requires good judgement to get reasonable information. Transparent to the user, the  $G'$ ,  $G''$  data is transformed to  $G(t)$ , so that Equation (5) can be used directly. As mentioned in the previous paragraph,  $G'$ ,  $G''$  data from oscillatory flow and creep/recoil measurements were combined. The fit was accomplished by assuming a functional form to the MWD function  $w(M)$ . The form could be either the Schulz-Flory or “Log Normal” distributions. One must also choose whether two terms (bimodal distribution) or one term (unimodal distribution) of the distribution functions are needed to describe the data. Empirically, one then chooses the approach which minimizes the error. If the error was not reduced by using two terms of  $w(M)$ , one term was chosen by default. The adjustable parameters in the fitting operation are  $\overline{M}_W$  and  $\overline{M}_W/\overline{M}_N$ . One value of each parameter (4, in all) is needed for the bimodal distribution fit.

We will first directly compare the Mead approach using a Single Exponential kernel, with that of Tuminello, using the Step Function. The data to be evaluated in the “Old Polystyrene Data” section is described in more detail in Reference 14. This data has some faults and “New Polystyrene Data” was evaluated as well.

### (1) Old Polystyrene Data

The data in Table I summarizes our comparison of the Rheometrics and Tuminello methods for determining the MWD of well-characterized polystyrenes. The nearly monodisperse samples are designated by their peak MW. For example, 34K refers to a narrow distribution sample with peak MW of 34,000 Da. The SEC data was obtained using a refractive index detector. A broad distribution standard from NIST, National Institute of Standards and Technology (formerly known as NBS), was also evaluated and designated as NBS 706. It is currently known as SRM706. Three bimodal distribution blends were also analyzed and are designated by their nearly monodisperse components.

The three lowest MW, narrow distribution standards are better characterized by the Rheometric software, whose predicted polydispersity ratios,  $\overline{M}_W/\overline{M}_N$ , are much closer to those determined by SEC. The higher narrow distribution samples all had a disturbing extra peak or shoulder at the low MW end of the distribution. This is shown for sample 350K in Figure 2. Figure 2 is a plot of selected differential MWD functions where the data points represent SEC results, the broad lines are the Rheometric determinations and the narrow lines are those of the Tuminello/DuPont method. This peak or shoulder, on samples like 350K, is thought to be due to the overlap with the transition region and/or the lack of sensitivity of rheological measurements to the low MW side of the

distribution. The Rheometric determination of the MWD, as illustrated in Figure 2, is closer to the shape determined by SEC for this narrow distribution sample.

**Table I**

**Comparison of Weight Average MW and Polydispersity Ratio for Polystyrene by Rheometry (WHT & Rheom) and SEC**

Sample	$\bar{M}_W(\times 10^{-3})$			$\bar{M}_W/\bar{M}_N$		
	SEC <sup>1</sup>	WHT <sup>1</sup>	Rheom <sup>2</sup>	SEC <sup>1</sup>	WHT <sup>1</sup>	Rheom <sup>2</sup>
34K	32.4	32.9	30.3	1.06	1.26	1.10
68K	66.4	67.7	67.1	1.04	1.23	1.09
115K	124	120	123	1.03	1.30	1.16
350K	346	333	347	1.13	1.37	1.38
675K	627	646	682	1.20	1.54	1.60
1150K	774	813	861	1.85	1.97	1.84
NBS706	258	230	226	2.24	2.28	2.18
34+115K	74.8	80.1	75.1	1.53	1.56	1.39
34+1150K	435	462	395	6.37	5.83	4.72
115+1150K	426	458	428	2.60	2.74	2.65

<sup>1</sup>W. H. Tuminello, Reference 14.

<sup>2</sup>Calculated from the Rheometric Scientific software.

The  $\bar{M}_W$  of sample NBS706 was determined to be about 12% too low by both rheological techniques. As we will show later, this appears to be caused by a sizable portion of polymer whose MW is lower than  $M_c$ . Figure 2 shows that the Rheometric method gives a more realistic shape to the distribution for NBS706 than the DuPont method.

Looking at the two blends with the 34K component in Table I, we see that the Rheometric predictions for the polydispersity ratio are quite low. This is

Figure 2 - MWD Determined from DuPont and Rheometrics Software plus SEC for Broad Versus Narrow Distribution Polystyrene Standards

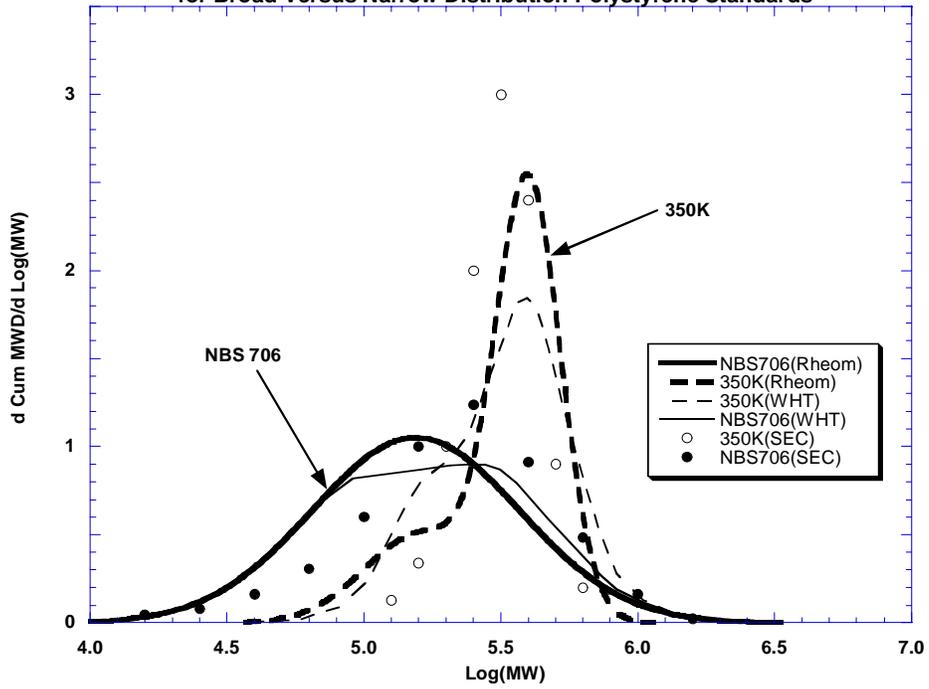
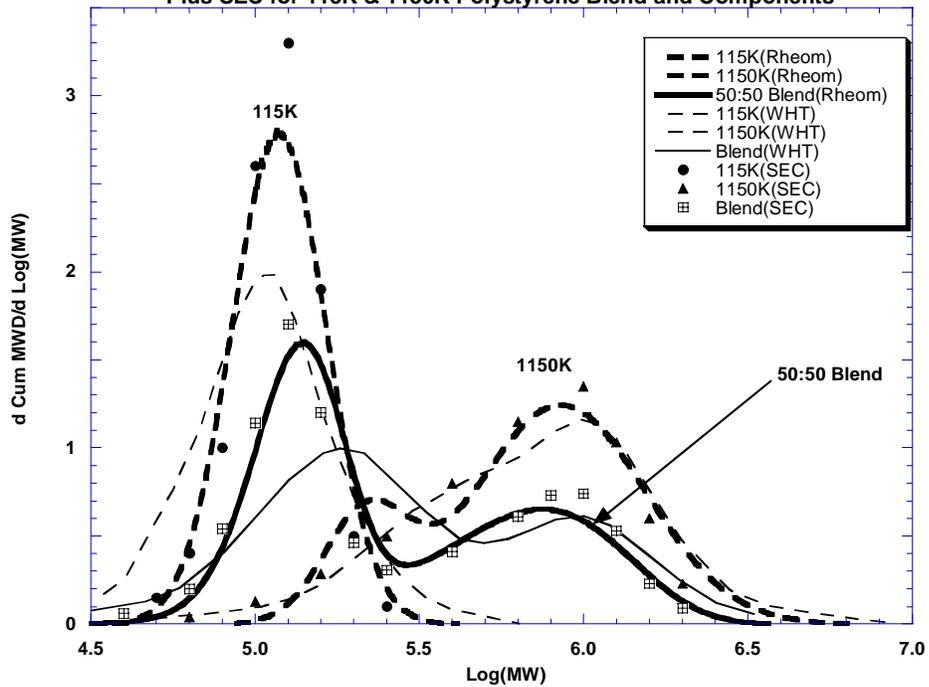


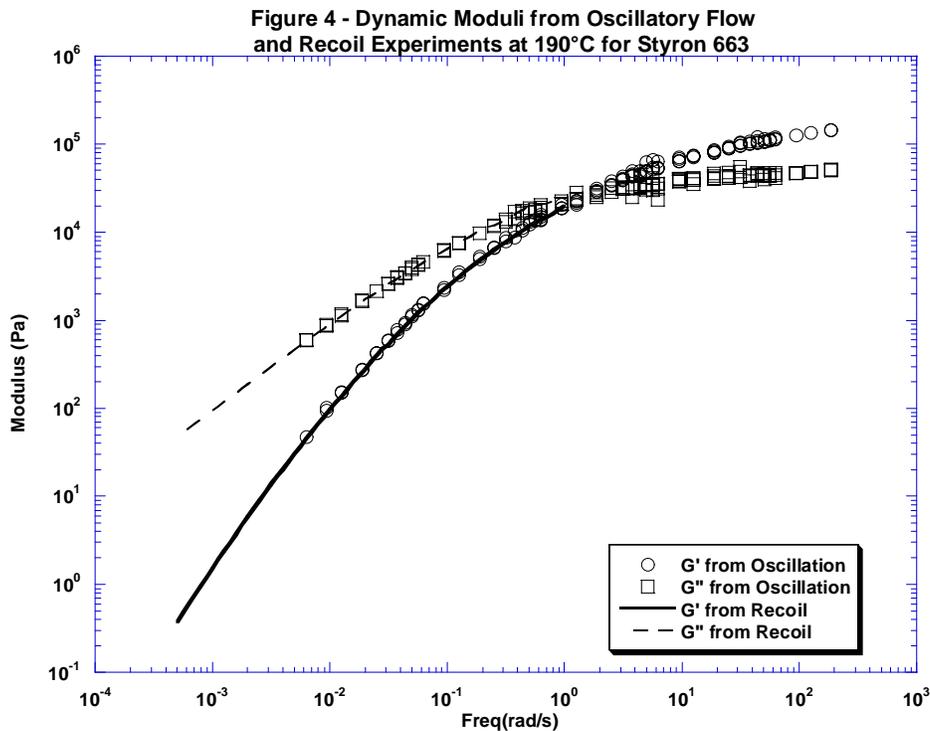
Figure 3 - MWD Determined from DuPont and Rheometrics Software Plus SEC for 115K & 1150K Polystyrene Blend and Components



probably due to the fact that the 34K sample is at the critical MW,  $M_c$ , and many of the model assumptions are inapplicable in this situation. This argument is strengthened when we look at the other blend whose low MW component has a MW of 115,000 Da. In this case, the predictions are well within the experimental error of the SEC data. The differential distributions of these blends are illustrated in Figure 3. In this figure, it is evident that the Mead model predictions for the narrow distribution sample and the bimodal blend are much closer to those predicted by SEC than the Tuminello/DuPont model which used the step-function kernel.

(2) New Polystyrene Data

There were some deficiencies in the “Old Data” that we wished to correct to strengthen the evaluation procedure. The “Old Data” was collected on a Rheometrics System IV rheometer. The apparatus had a convection oven with which temperature control of  $\pm 1^\circ\text{C}$  was difficult to maintain. The new rheometer was a Bohlin controlled stress apparatus with electrically heated plates with which we were able to maintain  $\pm 0.1^\circ\text{C}$  control with maximum gradients of the



same order. Better SEC data is now available by use of the previously mentioned MALS and viscometry detectors in addition to the traditional RI, refractive index, detector. The “Old Data” was collected only in oscillatory flow while some of the “New Data” was collected in the creep/recoil mode thus allowing access to lower rate data on which small amounts of high MW components can have a major effect. Figure 4 is an illustration of how the low

frequency portion of the dynamic moduli plots can be extended by more than an order of magnitude using recoil data. The polymer is a commercial polystyrene (Styron 663) from the Dow Chemical Company.

**Table II**  
**Comparison of Rheometric Determination of MWD with SEC**

	SEC*			Rheometric		
	$\bar{M}_Z$	$\bar{M}_W$	$\bar{M}_N$	$\bar{M}_Z$	$\bar{M}_W$	$\bar{M}_N$
220K	214000	206000	196000	234000	215000	196000
275K	275000	258000	242000	297000	261000	225000
Styron 663	443000	280000	142000	502000	275000	139000
NBS 706	409000	265000	143000	358000	201000	84100

\*Data of P. Cotts using MALS and RI detectors.

Table II and Figure 5 summarize the results of analyzing other polystyrenes which were characterized by SEC. The samples labelled 220K and 275K are nearly monodisperse samples from Polymer Laboratories. The numbers refer to the peak MWs as determined by Polymer Labs. Although the graphic representation of the distributions from SEC and rheometry does not show close agreement, the tabulated data shows agreement within about 10%. In fact, the polydispersity ratios,  $\bar{M}_W / \bar{M}_N$ , agree well within 10% which is acceptable for SEC results between laboratories.

NBS 706 was reanalyzed, both by SEC and rheometry. The results are shown in Table II plus Figures 6 and 7. It is obvious from Figure 6 that care and good judgement must be taken when interpreting data. Two different fitting approaches give low errors and the discrepancies in the fits occur at high frequencies where there is no data. This leaves some ambiguity in terms of the low MW end of the distribution. The high MW end is very reproducible with little ambiguity, however, as shown in Figure 7. This is fortunate, since this end of the distribution has the greatest affect on polymer processability. Also, the MW averages are quite a bit lower for the Rheometric determination in comparison with SEC. This is consistent with the findings of Boni and Sliemers<sup>20</sup> that NBS 706 has a sizeable fraction of oligomeric component (<30,000 MW) which acts as a plasticizer.

To this point we have compared the rheological findings with those of SEC, assuming the latter is the standard by which comparisons should be made.

Figure 5 - Comparison of Differential MWD Determined from Rheometry and SEC

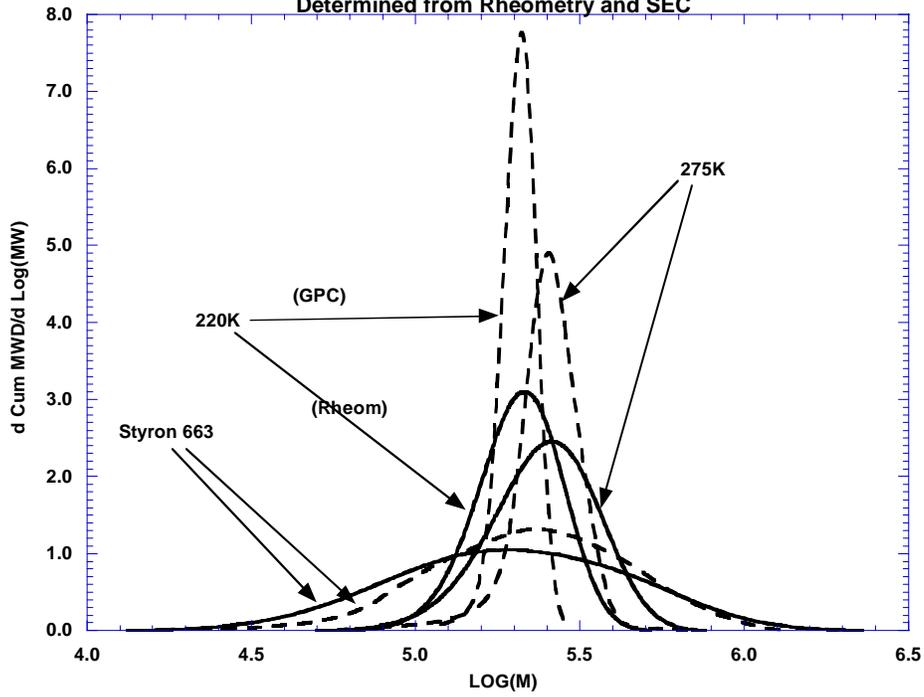


Figure 6 - Comparison of Schulz and Bimodal Fits for Dynamic Moduli of NBS706 at 160°C

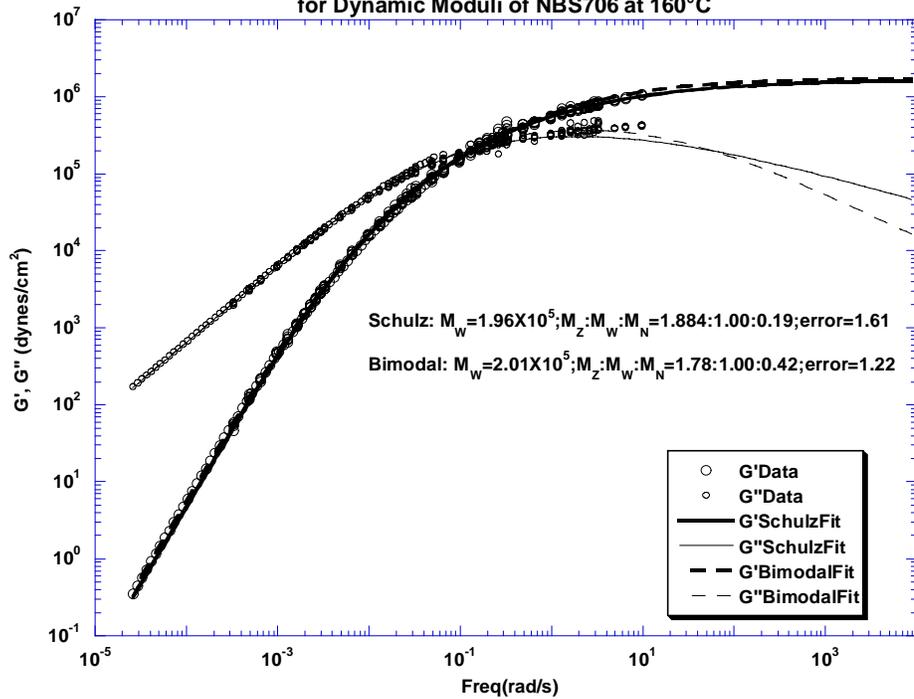
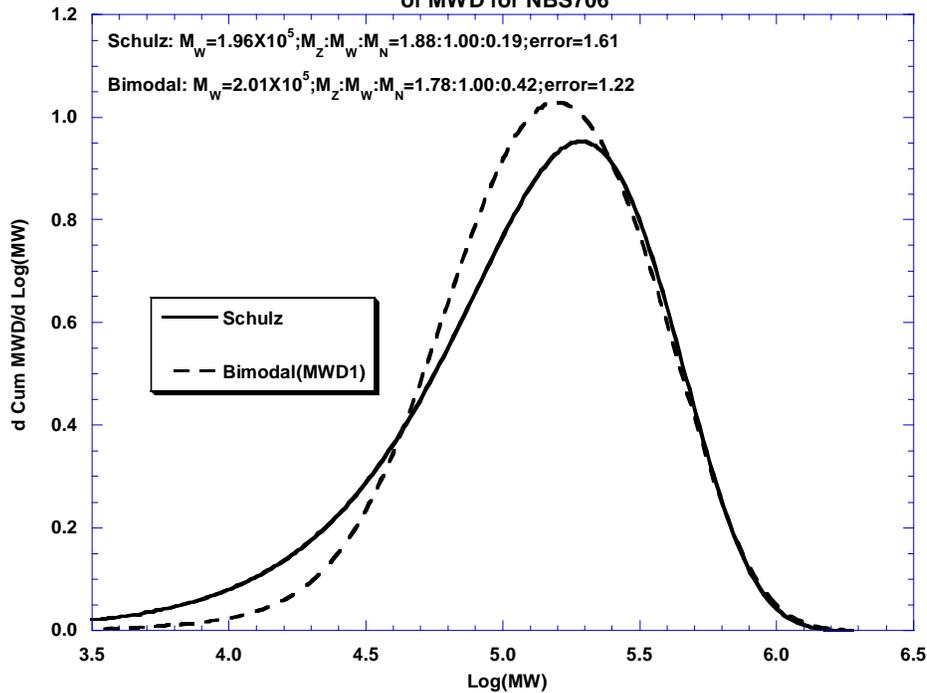


Figure 7 - Comparison of Schulz and Bimodal Rheometric Predictions of MWD for NBS706



However, there is some concern about the accuracy of SEC. To address this, Wasserman and Graessley<sup>11</sup> prepared two broad distribution polystyrenes from nearly monodisperse components by solution blending. The components of these two samples, M1 and M2, are listed in Table III. Assuming a “log normal” distribution for each component, the MWDs were constructed for each blend and are shown in Figure 8 with their calculated MW averages. The only difference between the samples is a slightly greater amount of high MW component for M2.

The dynamic moduli were determined from oscillatory flow and creep/recoil measurements in our laboratories. The results of the best fits to the data are shown in Figure 9. There is a dramatic difference in the storage moduli with such a small difference in MWD. The resulting MWDs from the fits shown in Figure 9 are illustrated in Figure 10. In Figure 11, the MWDs for sample M2 determined by SEC and rheology are compared with the calculated distribution. The SEC determination is quite close to that calculated but the rheological determination lacks the resolution. The latter is probably due to the very high precision and accuracy required (maybe unrealistically high) of the rheological data to get such resolution when the inverse operation of determining the MWD function from Equation (5) is used.

Although, we generally support the use of the Mead approach in determining the MWD from rheological data, there is a disturbing feature. One can use the Rheometric software to determine the dynamic viscoelastic properties

**Table III**

**Solution Blended Broad Distribution Polystyrenes\***

component	$M_i$ (X10 <sup>-5</sup> ) ( $M_p$ , Tosoh)	M1**	M2**
1	0.0298	0.001	0.001
2	0.0557	0.002	0.002
3	0.0910	0.004	0.004
4	0.1960	0.008	0.008
5	0.379	0.030	0.030
6	0.964	0.150	0.148
7	1.90	0.260	0.257
8	3.55	0.358	0.353
9	7.06	0.140	0.139
10	10.9	0.039	0.038
11	28.9	0.008	0.010
12	38.4	---	0.007
13	44.8	---	0.003

\*Wasserman & Graessley<sup>11</sup> \*\*weight fraction

from a given MWD. Keeping the weight average MW constant and varying the polydispersity ratio,  $\overline{M}_W / \overline{M}_N$ , changes the value of the zero shear viscosity. Plots of the complex dynamic viscosity calculated in such a way are shown in Figure 12. The low rate viscosity clearly increases with polydispersity ratio. This obviously does not agree with the well-accepted proportional relationship between zero shear viscosity and the 3.4 power of the weight average MW.

**Future Work**

Improvements can still be made in the rheological prediction of MWDs of linear polymers. Better quantitative predictions of narrow, broad and multimodal distributions are possible. Also, there is the disturbing prediction that the zero shear viscosity increases with polydispersity ratio using Mead's model. Maier, et. al<sup>10</sup> have used the unique approach of empirically optimizing the exponent  $\beta$  in Equation (5) to a value of 3.84. The physics behind this is not clear and more work appears necessary to evaluate the worth of this approach. Marin<sup>21</sup> has indicated that by emphasizing more strongly the interactions between long and short chains, that zero shear viscosity is not a function of polydispersity and can be accurately predicted using mixing rules he and his coworkers have developed.

Figure 8 - Comparison of the Calculated MWD for Polystyrene Samples M1 and M2

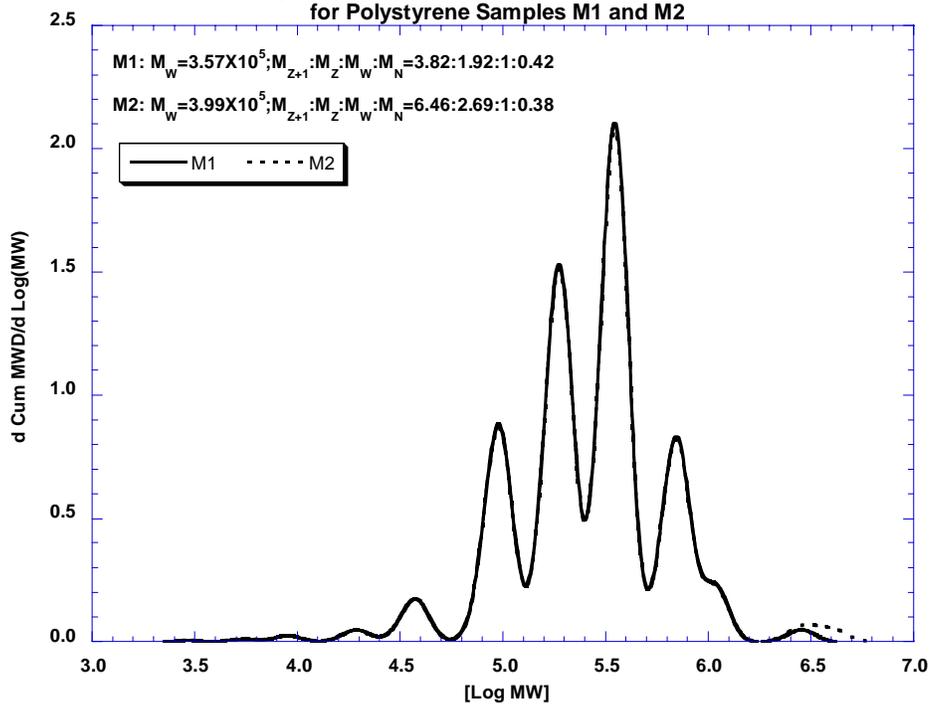


Figure 9 - Comparison of Dynamic Moduli for Polystyrene Samples M1 and M2 at 160°C

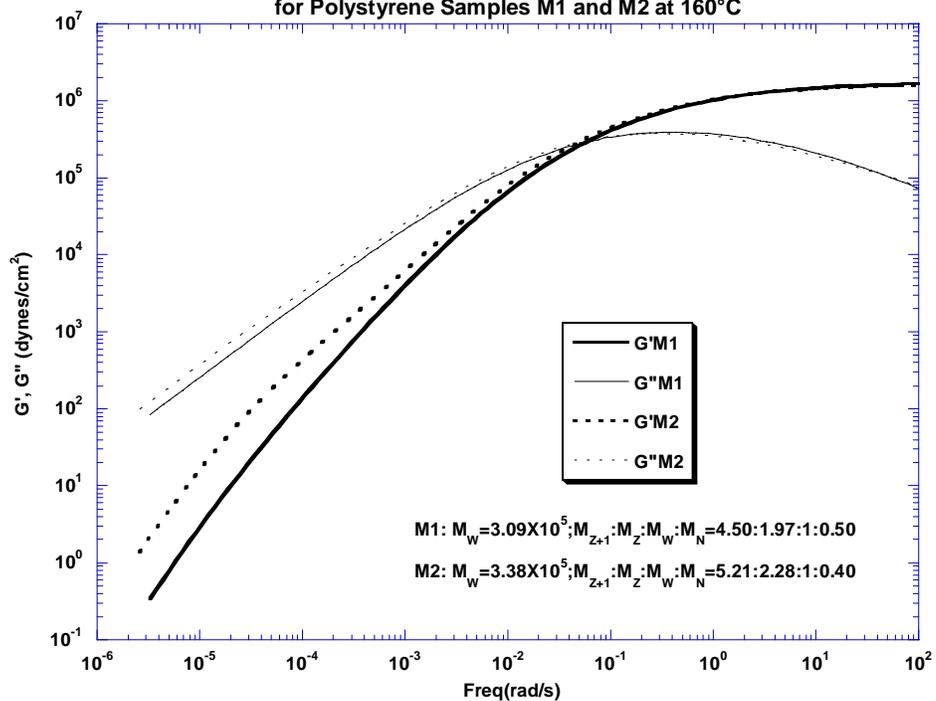


Figure 10 - Comparison of Differential MWDs for Polystyrene Blends M1 and M2 Determined from Rheometric Software

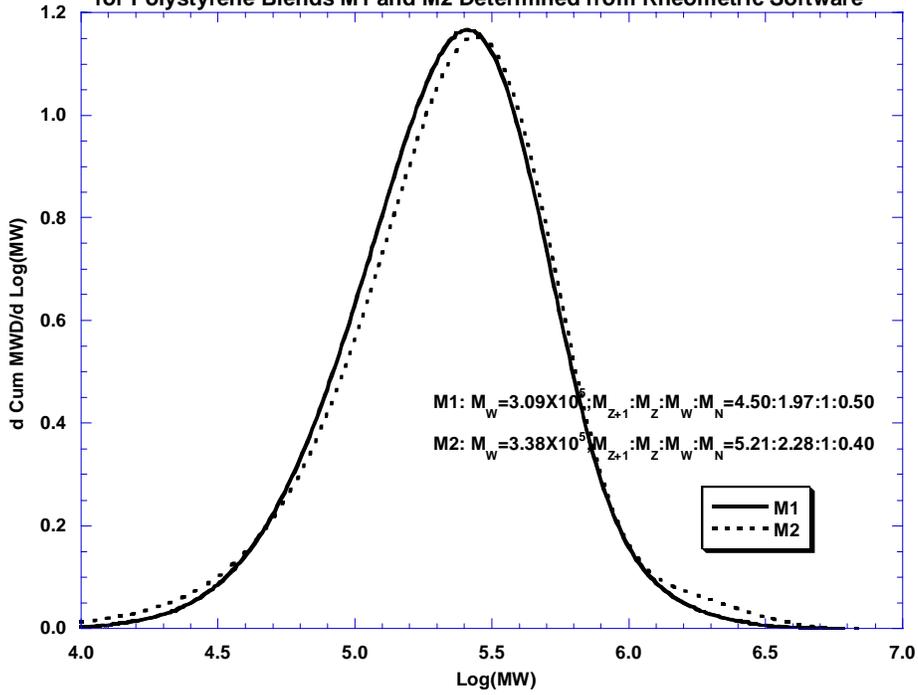
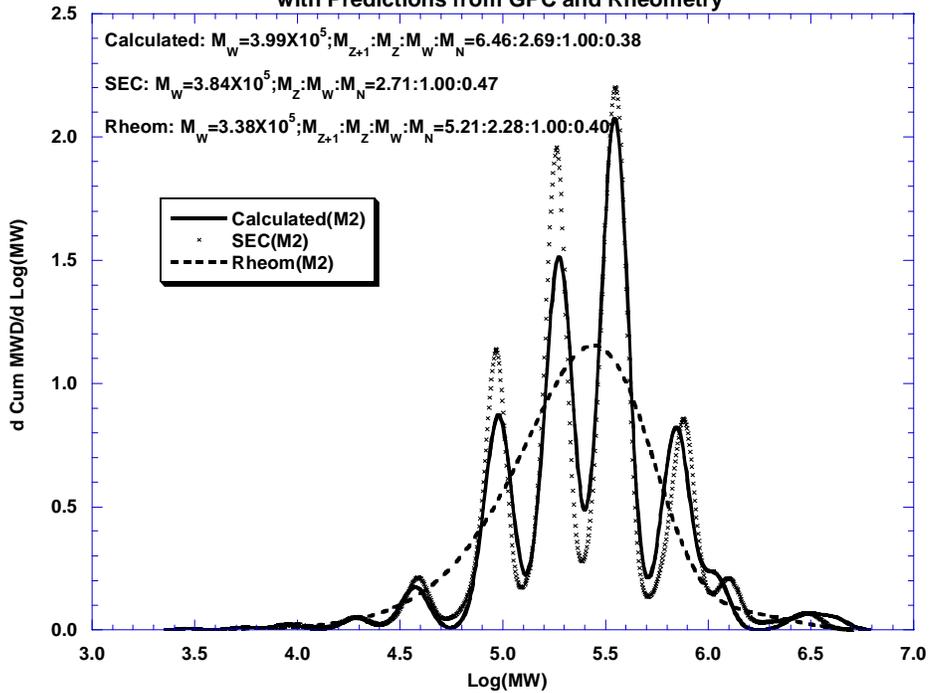
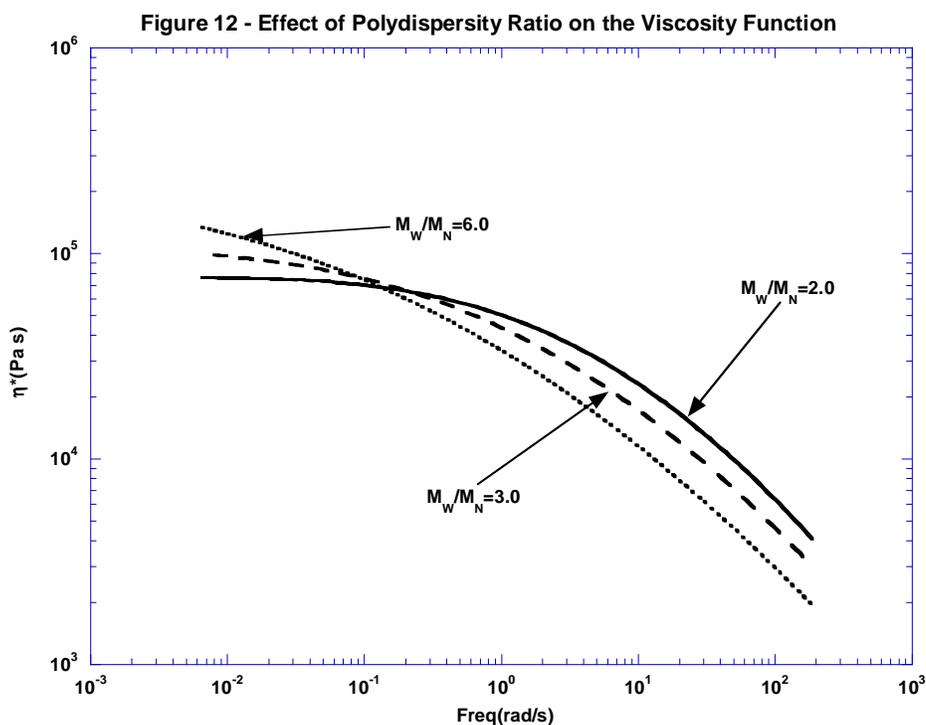


Figure 11 - Comparison of the Calculated MWD for Polystyrene Sample M2 with Predictions from GPC and Rheometry





Determining the molecular weight distribution of polymers with LCB has thus far proven elusive although much recent progress has been made. The most prolific worker in developing constitutive equations to account for the effects of LCB has been McLeish, whose publications in this area are too numerous to list, but one of the most recent articles is referenced.<sup>22</sup> Kasehagen and Macosko<sup>9</sup> have also done interesting work in this area. A very important contribution has been made by Janzen and Colby.<sup>4</sup> They have developed a Cayley Tree model through which the average amount of LCB can be determined using only the zero shear viscosity and the weight average MW from SEC. With this recent progress, I am confident that the elusive problem of characterizing the MWD and LCB in polyethylene is not far from being solved.

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