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Polymer 48 (2007) 2362–2370

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A rheology theory and method on polydispersity and polymer long-chain branching

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Received 15 September 2006; received in revised form 21 January 2007; accepted 22 January 2007
Available online 13 February 2007

Abstract

Model calculations were performed to investigate the sensitivity of zero-shear melt viscosity (η_0 or Eta0) on the molecular weight (MW) polydispersity of linear polymers. Simulated MW distributions (MWD) were generated with the generalized exponential (GEX) distribution function for various levels of polydispersity M_w/M_n and M_z/M_w. For linear entangled polymeric chains in the melt, the linear viscoelastic properties were predicted by using the double reptation blending rule and the so-called BSW relaxation time spectrum, named after the authors: Baumgaertel, Schausberger and Winter [Baumgaertel M, Schausberger A, Winter HH. Rheol Acta 1990;29:400–8]. Published rheological parameters appropriate for polyethylene were used in the calculations. It was found that Eta0 depended mostly on M_w, but it also significantly depended on the extent of high-MW polydispersity M_z/M_w. A revision to the fundamental MW dependency of Eta0 was proposed to compensate for this polydispersity effect. To offset the polymer polydispersity differences, we propose a new MW average (M_{HV} or M_x with $x = 1.5$) to replace M_w in the historical rheological power-law equation of Eta0 $\propto M_w^a$, where the literature value of exponent "a" ranges from 3.2 to 3.6. The use of M_{HV} instead of M_w in the power-law equation made the calculated Eta0 independent of the sample high-MW polydispersity. With the removal of the complication from polydispersity effect, the new Eta0 power law can now provide a more robust base for studying polymer long-chain branching (LCB). A new LCB index is thus proposed based on this new melt-viscosity power law. The values of M_{HV} in the new power law can be calculated for polymer samples from the conventional gel permeation chromatographic (GPC) slice data.

Keywords: Rheology; MWD; Long-chain branching

1. Introduction

It is well known that the rheological properties of polymer melts are strongly affected by the molecular weight (MW), molecular weight distribution (MWD) and long-chain branching (LCB) [1–5]. Historically, zero-shear melt viscosity Eta0 has always been considered to be a function of the polymer weight-average molecular weight (M_w) for linear polymers [6]:

$$\text{Eta0} \equiv \eta_0 = K \times M_w^a \quad (\text{exponent "}a\text{" ranges from 3.2 to 3.6}) \tag{1}$$

One goal of this study is to elucidate the cause for the errors in Eq. (1) when it is applied to polymers with differences in MW polydispersity. For this purpose, a series of MWD profiles were generated, based on the so-called generalized exponential (GEX) distribution [7,8], having the M_w/M_n and M_z/M_w values varied systematically. The Eta0 values were then calculated by using the approach described previously by Steeman [8]. Specifically, we used (1) the double reptation blending rule [9,10] and (2) the so-called BSW monodisperse relaxation time spectrum [11–13]. The details of the calculations are described below.

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doi:10.1016/j.polymer.2007.01.073

2. Methods

2.1. MWD simulation using the GEX function

The MWD curves were generated with the generalized exponential (GEX) distribution model [7]:

$$\text{GEX: } w(M) = \frac{mt^{(k+1)/m}}{\Gamma[(k+1)/m]} M^k \exp(-tM^m) \tag{2}$$

with

$$M_\text{n} = \Gamma[(k+1)/m]/t^{1/m}\Gamma[k/m] \tag{3}$$

$$M_\text{w} = \Gamma[(k+2)/m]/t^{1/m}\Gamma[(k+1)/m] \tag{4}$$

and

$$M_\text{z} = \Gamma[(k+3)/m]/t^{1/m}\Gamma[(k+2)/m] \tag{5}$$

In this study, all simulated distributions were generated with $k = 1$ and the polydispersity M_w/M_n (Pd) values of 2, 3, 5, 10, 15 and 20, with the corresponding high-MW polydispersity M_z/M_w values of 1.50, 1.96, 2.74, 4.30, 5.59 and 6.75, respectively (shown in the first and last column of Tables 1–4).

2.2. Eta0 calculation from MWD

First, the so-called BSW monodisperse relaxation time spectrum was used to associate it with the single MW species [11]:

$$H(M,\tau) = H_\text{f}\tau^n \times h(1 - \tau/\tau_\text{max}) \tag{6}$$

with

$$H_\text{f} = \frac{nG_n^0}{(\tau_\text{max})^n}$$

and

$$\tau_\text{max} = \left(\frac{1+n}{n}\right)\frac{\text{Eta0}(M)}{G_n^0}$$

This power-law relaxation time spectrum contains three parameters: (1) the pre-factor H_f, which normalizes the spectrum and is proportional to the equilibrium modulus G_n^0, (2) the relaxation time power-law exponent n, and (3) the maximum relaxation time $\tau_\text{max}(M)$, where the expression h in Eq. (6) is the Heaviside function.

Next, the stress relaxation modulus $G(M,t)$ is calculated by integration over the relaxation time spectrum:

$$G(M,t) = \int_0^{\tau_\text{max}} \frac{H(M,\tau)}{\tau} e^{-\frac{t}{\tau}} d\tau \tag{7}$$

Then, the stress relaxation curves of the various nearly monodisperse fractions $G(M,t)$ are blended into the bulk stress relaxation curve $G(t)$ of the polydisperse distribution $w(M)$ with the double reptation blending law [9,10]:

$$G(t) = \left[\int w(M)\sqrt{G(M,t)}dM\right]^2$$
$$\text{with } w(M) = \text{weight fraction at } M \tag{8}$$

Finally, the zero-shear melt viscosity Eta0 is calculated directly from the integration of the relaxation modulus [6]:

$$\eta_0 = \int_0^\infty G(t)\,dt \tag{9}$$

For the purpose of illustration, the rheological parameters of polyethylene reported by Wasserman and Graessley [12,13] were used in the following test case calculations.

Table 1
Polydispersity effect on melt viscosity at low shear rate – results of a theoretical study built on a GEX–MWD model with $a = 3.6$

Pd (M_w/M_n)	M_x	M_z	M_w	M_n	Eta0	M_z/M_w
Test case 1						
2	120,000	180,000	**120,000**	60,000	**7.08E + 04**	1.50
3	120,000	235,198	**120,000**	40,000	**9.09E + 04**	1.96
5	120,000	328,393	**120,000**	24,000	**1.31E + 05**	2.74
10	120,000	515,736	**120,000**	12,000	**2.19E + 05**	4.30
15	120,000	671,374	**120,000**	8000	**2.91E + 05**	5.59
20	120,000	809,465	**120,000**	6000	**3.50E + 05**	6.75
Test case 2						
2	**350,000**	428,661	285,774	142,887	**1.64E + 06**	1.50
3	**350,000**	489,998	250,001	83,334	**1.29E + 06**	1.96
5	**350,000**	578,994	211,574	42,315	**1.01E + 06**	2.74
10	**350,000**	725,590	168,828	16,883	**7.29E + 05**	4.30
15	**350,000**	827,865	147,971	9865	**5.98E + 05**	5.59
20	**350,000**	909,026	134,760	6738	**5.16E + 05**	6.75

Test case 1: errors from polydispersity on melt-viscosity power law $\text{Eta0} = K \times M_\text{w}^{3.6}$, $M_x = 120{,}000$ is held constant with MWD of varying Pd [for $x = 1$, $M_x = M_\text{w}$, and with $\text{Pd} = 2$ at $x = 1$, MWD = Flory most probable MWD].
Test case 2: over-compensation for polydispersity effect using $\text{Eta0} = K \times M_x^{3.6}$ with $x = 2$, $M_x = 350{,}000$ is held constant with MWD of varying Pd [for $x = 2$, $M_x = (M_\text{z} \times M_\text{w})^{0.5} = M_\text{w} \times (M_z/M_\text{w})^{0.5}$, or $\text{Eta0} \sim M_x^{3.6} \sim (M_\text{w}^{3.6}) \times (M_z/M_\text{w})^{1.8}$].

Table 2
Polydispersity effects on melt viscosity at low shear rate – results of a theoretical study built on a GEX–MWD model with $a = 3.6$

Pd (M_w/M_n)	M_x	M_z	M_w	M_n	Eta0	M_z/M_w
Test case 1						
2	120,000	180,000	**120,000**	60,000	**7.08E + 04**	1.50
3	120,000	235,198	**120,000**	40,000	**9.09E + 04**	1.96
5	120,000	328,393	**120,000**	24,000	**1.31E + 05**	2.74
10	120,000	515,736	**120,000**	12,000	**2.19E + 05**	4.30
15	120,000	671,374	**120,000**	8,000	**2.91E + 05**	5.59
20	120,000	809,465	**120,000**	6,000	**3.50E + 05**	6.75
Test case 3						
2	**200,000**	269,422	179,615	89,807	**3.05E + 05**	1.50
3	**200,000**	328,148	167,424	55,808	**3.04E + 05**	1.96
5	**200,000**	419,677	153,357	30,671	**3.17E + 05**	2.74
10	**200,000**	585,322	136,191	13,619	**3.43E + 05**	4.30
15	**200,000**	710,900	127,065	8471	**3.55E + 05**	5.59
20	**200,000**	815,977	120,965	6048	**3.59E + 05**	6.75

Test case 1: errors from polydispersity on melt-viscosity power law Eta0 $= K \times M_w^{3.6}$, $M_x = 120{,}000$ is held constant with MWD of varying Pd [for $x = 1$, $M_x = M_w$, and with Pd $= 2$ at $x = 1$, MWD = Flory most probable MWD].
Test case 3: adequate compensation for polydispersity effect using Eta0 $= K \times M_x^{3.6}$ with $x = 1.5$, $M_x = 200{,}000$ is held constant with MWD of varying Pd [for $x = 1.5$, $M_x = M_w \times (M_z/M_w)^{0.2635}$, or Eta0 $\sim M_x^{3.6} \sim (M_w^{3.6}) \times (M_z/M_w)^{0.95}$].

Table 3
Polydispersity effects on melt viscosity at low shear rate – result of a theoretical study built on a GEX–MWD model with $a = 3.2$

Pd (M_w/M_n)	M_x	M_z	M_w	M_n	Eta0	M_z/M_w
Test case 4						
2	120,000	180,000	**120,000**	60,000	5.10E + 04	1.50
3	120,000	235,198	**120,000**	40,000	5.94E + 04	1.96
5	120,000	328,393	**120,000**	24,000	7.48E + 04	2.74
10	120,000	515,736	**120,000**	12,000	1.04E + 05	4.30
15	120,000	671,374	**120,000**	8000	1.27E + 05	5.59
20	120,000	809,465	**120,000**	6000	1.46E + 05	6.75
Test case 5						
2	**200,000**	269,422	179,615	89,807	**1.88E + 05**	1.50
3	**200,000**	328,148	167,424	55,808	**1.88E + 05**	1.96
5	**200,000**	419,677	153,357	30,671	**1.77E + 05**	2.74
10	**200,000**	585,322	136,191	13,619	**1.65E + 05**	4.30
15	**200,000**	710,900	127,065	8471	**1.52E + 05**	5.59
20	**200,000**	815,977	120,965	6048	**1.50E + 05**	6.75

Test case 4: errors from polydispersity on the equation Eta0 $= K \times M_w^{3.2}$, $M_w = 120{,}000$ is held constant with MWD of varying Pd (for $x = 1$, $M_x = M_w$) (at Pd $= 2$, MWD = Flory).
Test case 5: adequate compensation for polydispersity effect using Eta0 $= K \times M_x^{3.2}$ with $x = 1.5$, $M_x = 200{,}000$ is held constant with MWD of varying Pd (at $x = 1.5$, high-MW tail is adequately compensated for).

These include the BSW relaxation time power-law exponent with the "n" value of 0.56 and the Eta0–M_w formulation of:

$$\eta_0 = 3.40 \times 10^{-14} M_w^{3.6} \text{ poise} \quad (190\,^\circ\text{C}) \tag{10}$$

and

$$G_n^0 = 2.3 \times 10^7 \text{ dyne/cm}^2 \tag{11}$$

3. Test case 1

3.1. Effect of polydispersity on Eta0 for GEX–MWD curves having constant M_w

In this test study with the M_w value of 120,000 being held constant, a series of 6 GEX–MWD curves were generated ranging from M_w/M_n of 2 to 20, and M_z/M_w of 1.50 to 6.75, respectively, as shown in the overlay plot in Fig. 1. These MWD curves were then used to calculate Eta0 by going through the steps described above. The results are tabulated as "Test case 1" in Table 1, and plotted in Fig. 2.

One sees in Fig. 2, a large increase in Eta0 with the increase in MW polydispersity, as illustrated in the plot of Eta0 against both M_w/M_n and M_z/M_w. This increase in Eta0 with increasing polydispersity is obviously not adequately accounted for by the historical Eta0–M_w power law described in Eqs. (1) and (10). If the historical Eta0–M_w power law was accurate, the Eta0 values in Fig. 2 and test case 1 in Table 1 would remain constant across the various values of M_w/M_n and M_z/M_w in the x-axis.

At a closer look of this result, one can easily see the cause of the problem. When M_w being held constant, increasing polydispersity will have to create more high-MW tail in the

Table 4
Polydispersity effects on melt viscosity at low shear rate – result of a theoretical study built on a GEX–MWD model with $a = 3.4$

Pd (M_w/M_n)	M_x	M_z	M_w	M_n	Eta0	M_z/M_w
Test case 6						
2	120,000	180,000	**120,000**	60,000	**6.01E + 04**	1.50
3	120,000	235,198	**120,000**	40,000	**7.05E + 04**	1.96
5	120,000	328,393	**120,000**	24,000	**9.18E + 04**	2.74
10	120,000	515,736	**120,000**	12,000	**1.40E + 05**	4.30
15	120,000	671,374	**120,000**	8000	**1.81E + 05**	5.59
20	120,000	809,465	**120,000**	6000	**2.15E + 05**	6.75
Test case 7						
2	**200,000**	269,422	179,615	89,807	**2.30E + 05**	1.50
3	**200,000**	328,148	167,424	55,808	**2.15E + 05**	1.96
5	**200,000**	419,677	153,357	30,671	**2.11E + 05**	2.74
10	**200,000**	585,322	136,191	13,619	**2.15E + 05**	4.30
15	**200,000**	710,900	127,065	8471	**2.19E + 05**	5.59
20	**200,000**	815,977	120,965	6048	**2.21E + 05**	6.75

Test case 6: errors from polydispersity on the equation Eta0 = $K \times M_w^{3.4}$, $M_w = 120,000$ is held constant with MWD of varying Pd (for $x = 1$, $M_x = M_w$) (at Pd = 2, MWD = Flory).
Test case 7: adequate compensation for polydispersity effect using Eta0 = $K \times M_x^{3.4}$ with $x = 1.5$, $M_x = 200,000$ is held constant with MWD of varying Pd (at $x = 1.5$, high-MW tail is adequately compensated for).

MWD curves (see Fig. 1). This increase in high-MW tail seen in the figure was not adequately accounted for in Eqs. (1) and (10), where M_w is used in the formulation.

This problem of historical Eta0–M_w power law is not unique to our simulated curves. The problem had been commonly experienced with real polymer results [8,12,13].

It is obvious that this polydispersity-dependency problem of Eqs. (1) and (10) is detrimental to the fundamental understanding of polymer rheology. It is also detrimental to the accuracy of attempting to quantify polymer long-chain branching (LCB) from the rheological measurements. The following is a new approach that we propose to correct the problem.

4. Proposing a new generalized MW-average formulation

The results from the last test study show that there is a need to include a polydispersity modifier to Eq. (1) for compensating the effect of high-MW tail in polymers. The presence of high-MW tail in MWD causes high M_z/M_w values. The increase of M_z/M_w polydispersity is typically accompanied by an increase of M_w/M_n polydispersity, like that shown in Fig. 2. Evidence for the need of such polydispersity modifiers had been reported for real polymer samples by Steeman [8] and by Wasserman and Graessley [12,13], as cited below in Eqs. (12) and (13), respectively. What they have done is to show that there is an additional dependency of Eta0 on polymer polydispersity that was not accounted for in the historical Eta0 versus M_w power law. They did not, however, outline any method for correcting the problem.

$$\eta_0 = K \times M_w^a \left(\frac{M_w}{M_n}\right)^{0.24} \left(\frac{M_z}{M_w}\right)^{0.44} \qquad (12)\ [8]$$

$$\eta_0 = K \times M_w^a \left(\frac{M_z}{M_w}\right)^{1.0} \qquad (13)\ [12,13]$$

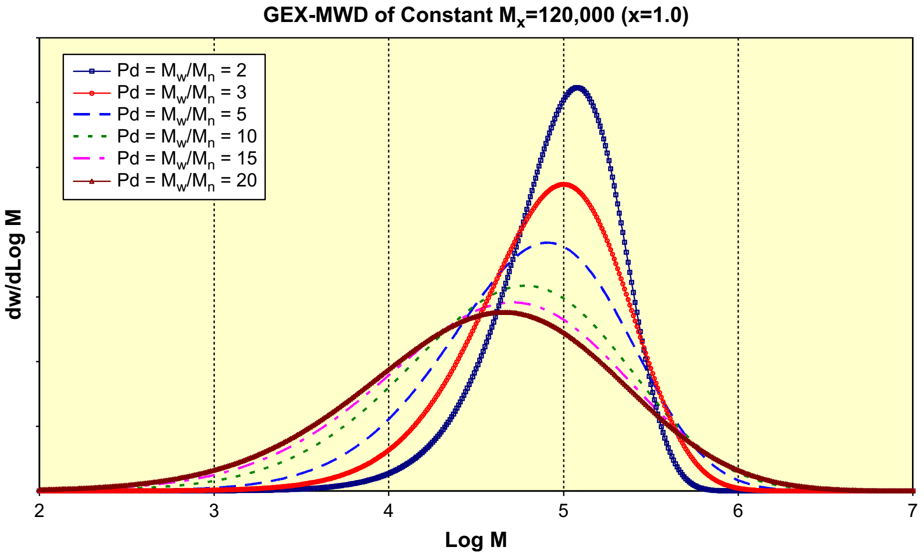

Fig. 1. GEX–MWD of constant $M_x = 120,000$ ($x = 1.0$).

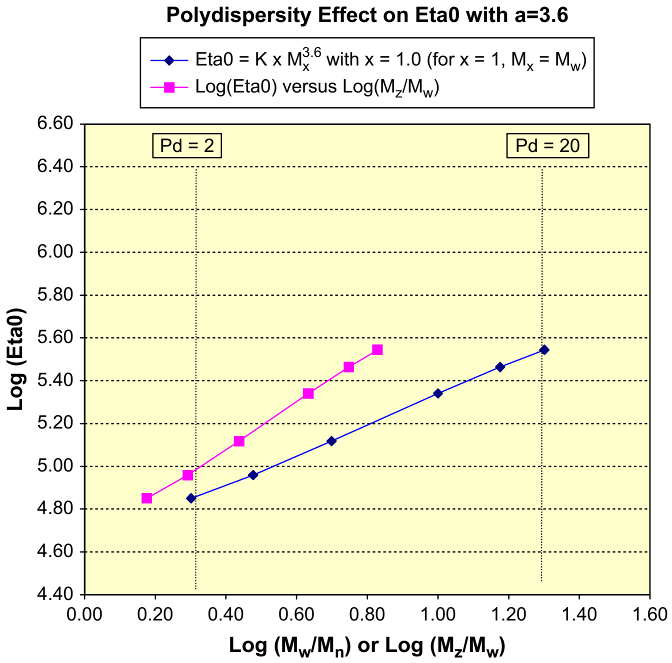

Fig. 2. Polydispersity effect on Eta0 with $a = 3.6$.

In an attempt to develop a practical method of compensating for this polydispersity effect in rheological measurements, we propose the use of a new statistical MW-average representation of M_x, as explained in the following equations. We define M_x as:

$$M_x \equiv \left[\frac{\sum_i w_i \times M_i^x}{\sum_i w_i}\right]^{\frac{1}{x}} \tag{14}$$

One can show that at some specific x values, the M_x parameter reduces to a neat function of the usual M_w and M_z values.

For example, for $x = 1$, we have:

$$M_{x=1} = \left[\frac{\sum_i w_i \times M_i^x}{\sum_i w_i}\right]^{\frac{1}{x}} = \left[\frac{\sum_i w_i \times M_i^1}{\sum_i w_i}\right]^{\frac{1}{1}} = M_w \tag{15}$$

and for $x = 2$, we have:

$$M_{x=2} = \left[\frac{\sum_i w_i \times M_i^2}{\sum_i w_i}\right]^{\frac{1}{2}} = \left[\left(\frac{\sum_i w_i \times M_i^2}{\sum_i w_i \times M^1}\right)\left(\frac{\sum_i w_i \times M_i^1}{\sum_i w_i}\right)\right]^{\frac{1}{2}}$$
$$= (M_z \times M_w)^{\frac{1}{2}} = M_w\left(\frac{M_z}{M_w}\right)^{\frac{1}{2}} \tag{16}$$

substituting $M_{x=2}$ for M_w in Eq. (1), and using $a = 3.6$ for example, we have:

$$\eta_0 = K \times M_{x=2}^{3.6} = K\left[(M_z M_w)^{\frac{1}{2}}\right]^{3.6} = K\left[\left(\frac{M_z}{M_w} M_w^2\right)^{\frac{1}{2}}\right]^{3.6}$$
$$= K \times M_w^{3.6}\left[\frac{M_z}{M_w}\right]^{1.8} \tag{17}$$

Notice that there is a close similarity between Eqs. (13) and (17), with the only difference being in the exponent value of the M_z/M_w modifier. Therefore, we see that the process of substituting M_x (*with a proper x value*) in Eq. (10) has the potential of becoming a tool to compensate for the polydispersity effect in the melt-viscosity power law.

5. Test case 2

5.1. A demonstration for an over-compensation example using M_x with $x = 2$

The method we propose to compensate for the polydispersity effect is to replace the M_w in the historical Eta0–M_w power law of Eq. (10) by a M_x average MW, defined earlier in Eq. (14). We see that an increase in the x value corresponds to an increase in the level of M_z/M_w polydispersity correction.

From the formulations described in the last section, we see that the effect of using $x = 2$ in M_x would be equivalent to the high-MW tail polydispersity correction factor of $(M_z/M_w)^{1.8}$ (with the assumed a value of 3.6 in the viscosity–MW power law). It is of interest to compare it to the factor of $(M_z/M_w)^{1.0}$ in Eq. (13) which has a lower exponent value of 1.0, derived from the experimental data of Wasserman and Graessley [12,13]. This lets us to believe that a compensation using $x = 2$ in M_x would result in an over-compensation situation. This is indeed what we observed in our simulation results of this test case 2 shown in Fig. 3 and Table 1.

In this test study, the M_x value at $x = 2$ of 350,000 was held constant in generating a series of 6 GEX–MWD curves with varying polydispersities ranging from M_w/M_n of 2 to 20, and M_z/M_w of 1.50 to 6.75, respectively. These MWD curves were then converted to the corresponding Eta0 values shown in Fig. 3 and Table 1. One sees from Fig. 3 that, with $x = 2$ and $a = 3.6$, the polydispersity effect in the MWD curves is now over-corrected. The polydispersity effect is now reversed from that of the original M_w situation. With $x = 2$, the Eta0 values are now turned into a trend of decreasing Eta0 with increasing polydispersity.

6. Test case 3

6.1. A proposal of using $x = 1.5$ in M_x for polydispersity compensation of Eta0

The method we propose to compensate for the polydispersity effect is to replace M_w in the historical Eta0–M_w power law of Eq. (10) by a M_x average MW using the value of $x = 1.5$.

In this test case study, the M_x value at $x = 1.5$ of 200,000 was held constant in generating a series of 6 GEX–MWD curves with varying polydispersities ranging from M_w/M_n of

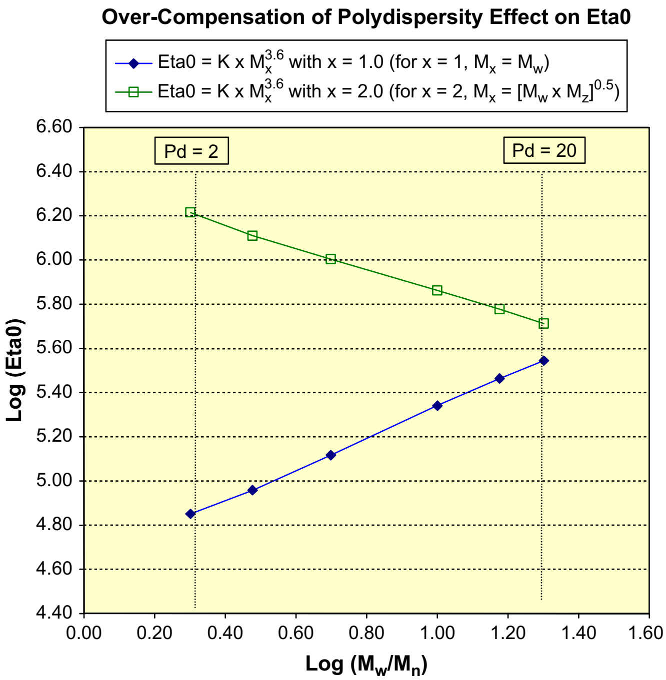

Fig. 3. Over-compensation of polydispersity effect on Eta0.

2 to 20, and M_z/M_w of 1.50 to 6.75, respectively. These MWD curves were then converted to the corresponding Eta0 values shown in Fig. 4 and Table 2.

One sees in Fig. 4 that with $x = 1.5$ in M_x, a convergence of the Eta0 values is approached that makes Eta0 nearly independent of the MW polydispersity values.

Since there is a range of reported exponent-a value that covers from 3.2 to 3.6, we decided to test this M_x correction approach for the lower exponent-a values of 3.2 and 3.4 also, as shown in our test cases 4 through 7 described below.

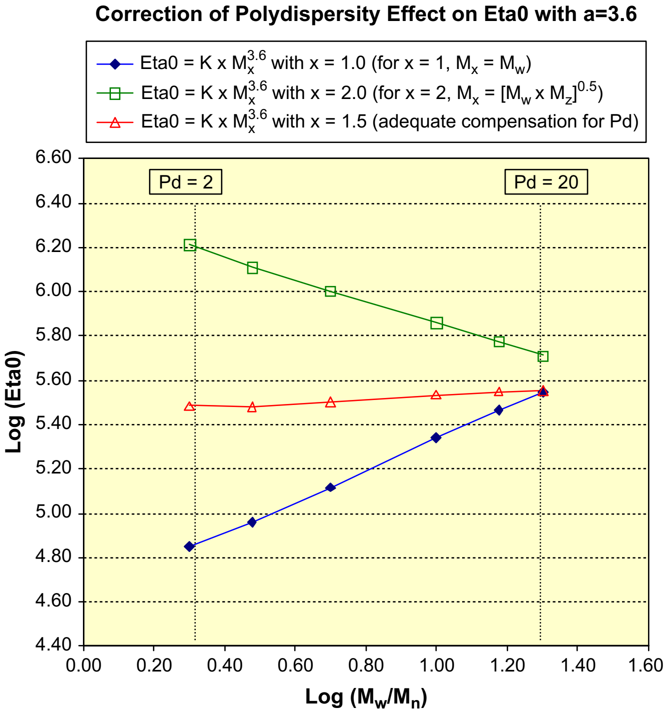

Fig. 4. Correction of polydispersity effect on Eta0 with $a = 3.6$.

7. Test case 4 through 7

7.1. Using $x = 1.5$ in M_x for polydispersity compensation of Eta0 at $a = 3.2$ and $a = 3.4$

The results of these test cases for $a = 3.2$ and $a = 3.4$ are shown in Figs. 5 and 6, and Tables 3 and 4. In both cases, the use of M_x at $x = 1.5$ is shown being also very successful of compensating for the polydispersity effect on Eta0. These additional test results provided the support for the proposed method being useful over the entire range of "a" values from 3.2 to 3.6.

In order to keep the calculated Eta0 values at different "a" values within a reasonable level, when we modified Eq. (10) to $a = 3.2$ and $a = 3.4$, we also made a change of the pre-factor K values to give:

$$\text{For } a = 3.2, \quad \eta_0 = 3.40 \times 10^{-12} M_w^{3.2} \tag{18}$$

$$\text{For } a = 3.4, \quad \eta_0 = 3.40 \times 10^{-13} M_w^{3.4} \tag{19}$$

8. More on the proposed method of compensating polydispersity in Eta0

For a simpler notation, we define:

$$M_{HV} \equiv M_x(\text{at } x = 1.5) = \left[\frac{\sum_i w_i \times M_i^{1.5}}{\sum_i w_i}\right]^{\frac{1}{1.5}} \tag{20}$$

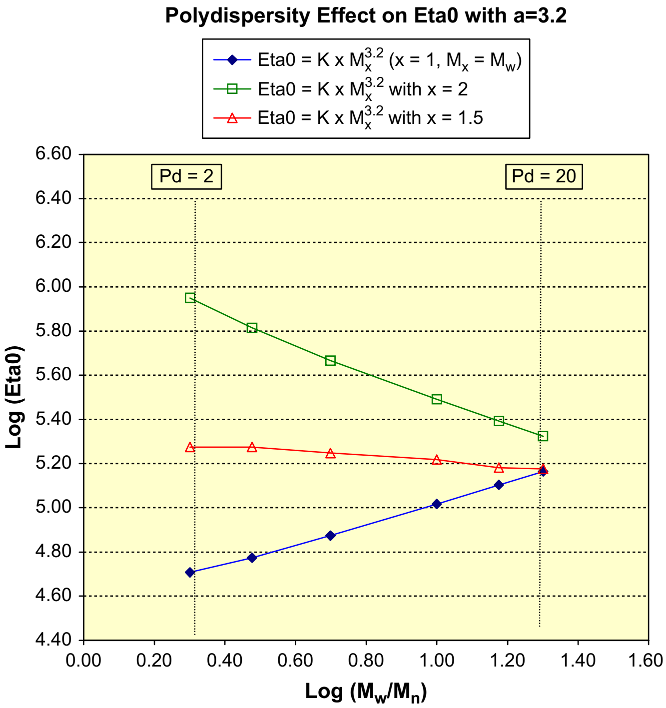

Fig. 5. Polydispersity effect on Eta0 with $a = 3.2$.

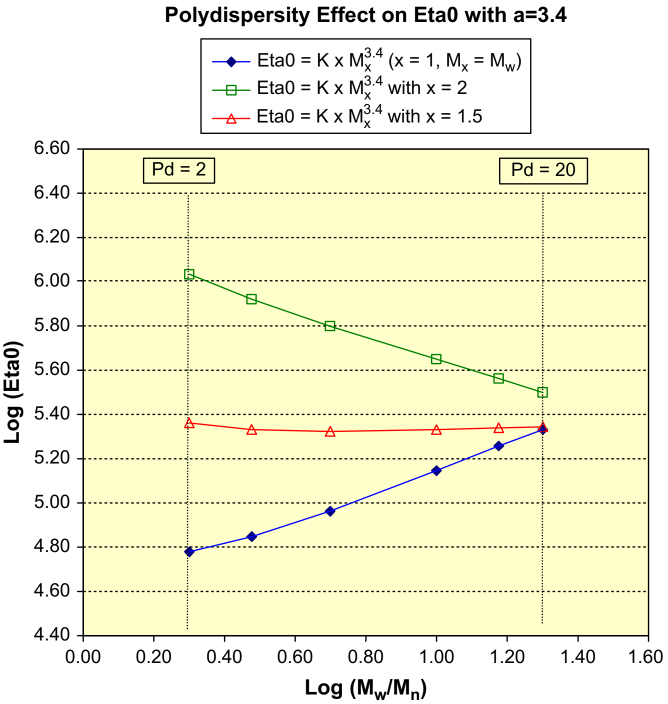

Fig. 6. Polydispersity effect on Eta0 with $a = 3.4$.

where M_{HV} may be referred to as the "hydrodynamic-volume average MW" for a reason to be explained later.

This formula of calculating M_{HV} can be easily carried out on existing GPC–MWD slice data with conventional MW calibration procedures. Incorporation of this formula into any GPC data processing modules can be easily done with very few processing code changes needed. Because of its lower MW exponent of 1.5 in Eq. (20) than the exponent value of 2 required in the M_z formulation, the precision of the M_{HV} value in the GPC experiment can be expected to be better than that of the M_z value, and closer to that of the M_w value.

We will now take a closer look of M_{HV} as defined in Eq. (20). We noticed that the exponent of 1.5 on MW is close to the MW dependency of polymer hydrodynamic volume (HV) on MW for the linear random coil polymers in the molten state. We have:

$$M_{HV} \equiv \left[\frac{\sum_i w_i \times M_i^{1.5}}{\sum_i w_i}\right]^{\frac{1}{1.5}} \approx \left[\frac{\sum_i w_i \times \mathrm{HV}_i}{\sum_i w_i}\right]^{\frac{1}{1.5}} \approx \left[\mathrm{HV}_{avg}\right]^{\frac{1}{1.5}} \tag{21}$$

where

$$\mathrm{HV}_i \approx \left(R_{g,i}\right)^3 \approx \left(M_i^{0.5}\right)^3 \approx M_i^{1.5} \quad \text{(for linear polymer)} \tag{22}$$

and R_g is the root-mean-square-radius of polymer molecules. For a linear polymer in the melt, this R_g parameter is expected to scale with the MW raised to the 0.5 power, under the excluded volume screening condition in polymer melt [14].

Substituting M_{HV} for M_w in Eq. (1), we have:

$$\eta_0 = K \times M_{HV}^a \approx K\left[\left[\mathrm{HV}_{avg}\right]^{\frac{1}{1.5}}\right]^a = K\left[\mathrm{HV}_{avg}\right]^{\frac{a}{1.5}} \approx K \times \mathrm{HV}_{avg}^{2+\left(\frac{a-3}{1.5}\right)} \tag{23}$$

It is interesting to speculate a little about the implication of the results in Eq. (23). It might appear to suggest that the hydrodynamic volume (or size) of the polymer molecule plays the basic role in melt viscosity of *linear polymers*, more so than the polymer MW per se. In Eq. (23), the exponent value of the ratio a/1.5 on the HV term ranges from about 2.1 to 2.4, depending on the exponent "a" values of 3.2 to 3.6, respectively. These values are close to the blending rule exponent value of 2 derived from the reported double reptation theory. This makes the blending rule exponent value of 2 easier to understand when HV is being considered as the basic contributing entity to the bulk melt viscosity of linear broad MWD polymers.

9. Relevancy of this work to LCB study

The accuracy and precision of the melt-viscosity power law are the foundation to the rheological methods of characterizing polymer LCB. One disturbing question of a persistent challenge is to know how to separate the effect of LCB on melt viscosity from that caused by the MW polydispersity effect. By way of this study of GEX–MWD modeling, we felt that we might be able to compensate for the polydispersity effect by the use of M_{HV} methodology of replacing M_w by M_{HV} in the historical power-law equation. It is hoped that by doing so, we can establish a more reliable power-law relationship to be used as the linear reference for the LCB studies. Hopefully, the LCB index proposed below can provide a useful addition to the existing rheological LCB methods [15,16] for studying the complex problem of polymer LCB.

Specifically, what we propose is to establish a power-law relationship for linear polymers by using M_{HV} instead of M_w to fit the MW information derived from GPC to the rheology Eta0 values. With that as the reference for linear polymers, we can study polymer LCB by using a LCB index defined in the following equation:

$$\text{“LCBI\_M}_{\text{HV}}\text{”} = \left(\left(\frac{\mathrm{Eta0}}{\mathrm{K_a}}\right)^{\frac{1}{a}} \Big/ \mathrm{M_{HV}}\right) - 1 \tag{24}$$

where Eta0 = experimental zero-shear melt viscosity of the current sample, M_{HV} = experimental GPC measured value of the current sample, K_a and a = the viscosity power law parameters with M_{HV}.

In all cases, the M_{HV} values should be calculated from conventional GPC calibration, not from the online light scattering detector or from online viscosity detector using universal calibration. The conventional GPC calibration provides the information of the polymer chain backbone's MW which is needed for relating to the rheological properties of a linear-equivalent structure.

10. Level of high-MW polydispersity compensation using M_{HV}

The GEX–MWD curves of holding a constant M_{HV} are shown in Fig. 7. By comparing it to Fig. 1 of $x = 1$ case, one can notice that the high-MW tail of the broader MWD curves became less pronounced in Fig. 7 with $x = 1.5$. This change we see is the result of the shifting of the broader MWD curves toward lower MW; this shift of the curves has the effect of compensating for the longer high-MW tail associated with broader MWD curves of higher polydispersity.

In order to quantify the level of polydispersity correction of M_x at different x values, we propose the use of the following empirical analysis. We let:

$$M_x = M_{\mathrm{w}} \left[\frac{M_{\mathrm{z}}}{M_{\mathrm{w}}}\right]^{y} \tag{25}$$

Therefore,

$$\eta_0 \approx M_x^a \approx M_{\mathrm{w}}^a \left[\frac{M_{\mathrm{z}}}{M_{\mathrm{w}}}\right]^{(a\times y)} \tag{26}$$

Where

$$\left[\frac{M_{\mathrm{z}}}{M_{\mathrm{w}}}\right]^{(a\times y)} \equiv \text{high-MW polydispersity compensation factor} \tag{27}$$

The exponent-y value in Eq. (26) can be estimated by the slope of the log–log plot of M_x/M_{w} versus $M_{\mathrm{z}}/M_{\mathrm{w}}$, as shown for $x = 3.6$ case in Fig. 8. From this plot, we obtained $y = 0$ in $x = 1$ case, and $y = 0.5$ in $x = 2$ case, as one would have expected from Eqs. (15) and (16), respectively. For $x = 1.5$, we obtained $y = 0.2635$. With the slope "y" values obtained from the trend line in Fig. 8, we have the following results:

For $x = 1.0$ and $a = 3.6$, we have:

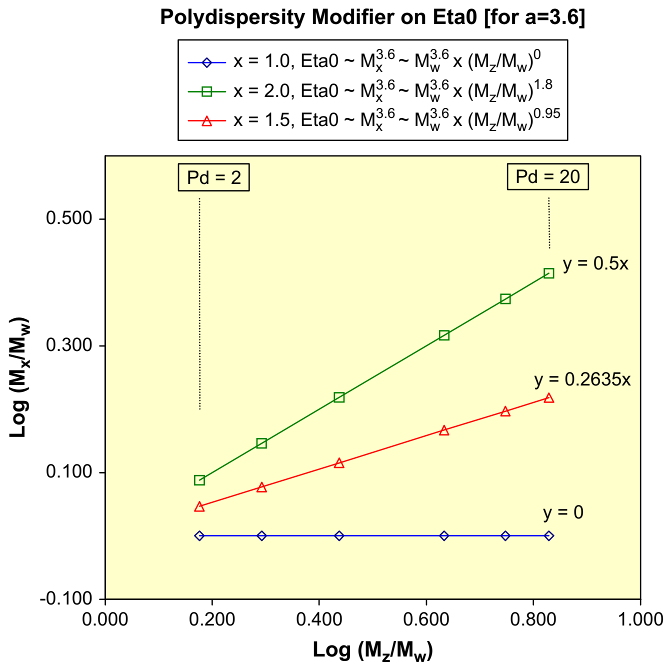

Fig. 8. Polydispersity modifier on Eta0 (for $a = 3.6$).

$$\eta_0 \approx M_x^{3.6} \approx M_{\mathrm{w}}^{3.6} \left[\frac{M_{\mathrm{z}}}{M_{\mathrm{w}}}\right]^{(3.6\times 0)} \approx M_{\mathrm{w}}^{3.6} \tag{28}$$

For $x = 2.0$ and $a = 3.6$, we have:

$$\eta_0 \approx M_x^{3.6} \approx M_{\mathrm{w}}^{3.6} \left[\frac{M_{\mathrm{z}}}{M_{\mathrm{w}}}\right]^{(3.6\times 0.5)} \approx M_{\mathrm{w}}^{3.6} \left[\frac{M_{\mathrm{z}}}{M_{\mathrm{w}}}\right]^{1.8} \tag{29}$$

(As expected, Eq. (29) turns out to be identical to that of Eq. (17).)

For $x = 1.5$ and $a = 3.6$, we have:

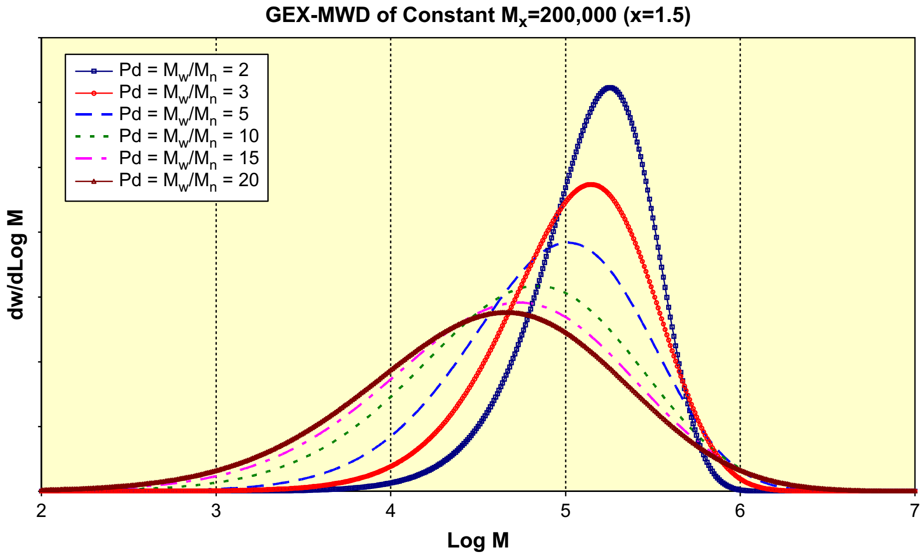

Fig. 7. GEX–MWD of constant $M_x = 200{,}000$ ($x = 1.5$).

$$\eta_0 \approx M_x^{3.6} \approx M_w^{3.6}\left[\frac{M_z}{M_w}\right]^{(3.6\times 0.2635)} \approx M_w^{3.6}\left[\frac{M_z}{M_w}\right]^{0.95} \tag{30}$$

It is interesting to note that the exponent value of 0.95 of the term M_z/M_w in Eq. (30) is very close to the value of 1.0 in Eq. (13) reported by Wasserman and Graessley based on their laboratory results on polyethylene samples [12]. This ''coincidental'' agreement provided an independent validation of the M_{HV} method we proposed in this work, for correcting the polydispersity effect in the melt-viscosity power law.

11. Discussions

1. The results of this GEX–MWD simulation study provided a quantitative way for examining the effect of MW polydispersity on the historical melt-viscosity power law which is based on the polymer weight-average MW (M_w).
2. Building from the lessons learned from the simulation study, we have proposed a method to correct for the polydispersity problem. Our method teaches: (1) the use of a new MW average M_{HV} defined as a hydrodynamic volume average MW, and (2) the use of this M_{HV} to replace M_w in the viscosity power-law equation.
3. This M_{HV} method was tested successfully with the GEX–MWD model which gives the usual bell-shaped MWD curves. It is recommended that this new method be tested against other simulation models that include bimodal MWD profiles.
4. It is also recommended that the proposed M_{HV} method be tested against the real data of linear polymer samples to establish the true exponent-*a* value and the pre-factor for the Eta0–M_{HV} power-law relationship for linear polymers. The accuracy of this experimental Eta0–M_{HV} calibration is the important building block for developing a robust LCB method using Eq. (24).
5. The accuracy of both the GPC–MWD analyses and the experimental Eta0 values is of course very important to the accuracy of the Eta0–M_{HV} power-law calibration, and therefore it is important to the accuracy of the proposed LCB method as well.
6. It is possible that the proposed M_x approach can be extended to provide polydispersity correction to other rheological measurements besides the zero-shear melt viscosity Eta0. To correct for polydispersity effect in melt index (MI) and high-load melt index (HLMI), we need to replace M_w by M_x with $x < 1$ for MI, and $x \ll 1$ for HLMI. In higher shear rate experiments, we need to have $x < 1$ to account for the contribution of the polydispersity effect in the low-MW region of MWD that is lower than M_w. Rheological parameters associated with higher shear rates are expected to relate to the MW average of M_x with a lower x value. It will be interesting to study how does this x-parameter in the M_x calculation responds as a function of shear rates in the rheological experiments.
7. *The term M_{HV} used in this paper is meant to apply to linear polymers*. It is not intended to imply that same rheological property should result from a long-chain branched polymer having the same M_{HV} of a linear polymer. A long-chain branched polymer of same hydrodynamic volume as a linear polymer could have much stronger effect on melt rheology due to enhanced entanglement, longer reptation time, etc. The size of the long-chain branched polymer is determined mostly by the polymer chain backbone length and MW. Therefore, the conventional GPC calibration should be used to calculate M_{HV}. For long-chain branched polymers, this value represents the linear-equivalent chain backbone M_{HV}.
8. For linear polymers, this M_{HV} parameter, which is readily measurable by GPC, could also possibly be useful for studying the propensity and population of inter-lamellae tie-molecule formation in semi-crystalline structures of polymer products.

Acknowledgements

The author wishes to acknowledge the support of Lyondell management for this work. The author wishes also to thank Jean Merrick-Mack, Clay Enos, Harry Mavridis and Natalia Nagy for their stimulating discussions during the course of this work.

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