

# Determining Molecular Weight Scale and Molecular Weight Distribution of Ethylene-Tetrafluoroethylene Alternating Copolymer via a Rheological Technique

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**ABSTRACT:** A self-scaling rheology-based technique was developed to determine the molecular weight (MW) and molecular weight distribution (MWD) of ethylene-tetrafluoroethylene alternating copolymer (ETFE). The self-scaling technique makes determining MW and MWD with isolated completely rheological method possible. Moreover, the two key parameters (the plateau modulus and zero-shear viscosity) were obtained by more robust numerical technique, which let determining MW and MWD via rheological method initiated by Tuminello [Macromolecules 1993, 26, 499] being building on more robust and rigid basis. Our case overcomes the shortage of Tuminello's method and gives more practical and simply mean to analyze the MW scale and MWD in the production and

application of ETFE. It is found that the peak MW of a ETFE (commercial grade: EP541) is  $1.73 \times 10^5$  g/mol, the MWD curve is a pattern with a slightly raised "shoulder" at high-molecular mass end, and a high peak on the median and the polydispersity is broad (the polydispersity index is near to 10.3). The wide polydispersity indicates the commercial ETFE combining good processability of relative lower MW molecules with physical properties of high MW ones. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2442–2448, 2012

**Key words:** ethylene-tetrafluoroethylene alternating copolymer; molecular weight; molecular weight distribution; dynamic rheology

## INTRODUCTION

With rapidly growing application in aerospace, offshore exploiting, and membrane structures in architecture now, we use more and more fluoropolymer for meeting the special requirements within these areas. Therefore, the desire to precisely characterize and then tailor modify fluorinated macromolecules is becoming more intensified. As a result, accurately determining molecular weight (MW) and its distribution (MWD) are also expected more. Practically, owing to the fundamental role in determining the physical performance and processability of polymers, MW and its distribution are, all the time, among the focuses of attention of polymer science and concerned industries.<sup>1,2</sup>

Many methods and techniques, such as gel permeation chromatography, end functional analysis, and laser light scattering (LLS), to name a few, have been used extensively in analysis and evaluation of MW and MWD. However, it is a pity that those

tools do not have effectiveness, even no ability, in MW and MWD determination of fluoropolymer due to their very poor solubility and extreme high-melt temperatures.<sup>3–6</sup> Rheometry is a potent replacement of common molar weight detection, and we do not need solving polymers, and it also works well under elevated temperatures.<sup>5</sup> Consequently, the mean is applied early in characterization of molar mass of fluororesin, such as Tuminello's work on MWD determination of ethylene-tetrafluoroethylene alternating copolymer (ETFE),<sup>7</sup> PTFE,<sup>8</sup> and FEP<sup>9</sup> based on rheology. Tuminello sees storage moduli of macromolecular fluid as the mirror of the cumulative MWD, and frequency axis can be scaled up with MW, and thereby rheology-based method could give out relative MWD of polymer fluid conveniently. If the absolute value of zero shear viscosity and molar mass average has known, the absolute MWD can also be calculated. However, Tuminello's work on determining of MWD of ETFE by rheology-based method would be more perfect if the following cloud such as (1) adopting simply the highest storage modulus measured as plateau modulus ( $G_N^0$ ), (2) depending on LLS (LLS) data to determine the proportionality constant ( $k$ ) between zero shear viscosity ( $\eta_0$ ) and MW, and (3) using experimental value

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without any numerical treatment as  $\eta_0$  are blown away. Because (1)  $G_N^0$  decides the breadth of MWD and a broader  $G_N^0$  gives a broader MWD calculated, and so a more precise  $G_N^0$  favors the accuracy of MWD calculated; (2) scaling toward the absolute MWD is key point for the robustness of the absolute value of MW and thus also MWD; and also (3) only being on the basis of exact  $\eta_0$ ,  $K$ , and MW, the absolute MWD could be scaled and calibrated. Although Tuminello attained  $\eta_0$  only by experimental measurement, experiment data may not be doubtless identical to the real  $\eta_0$  and then misleading the final outcome happens possibly. On  $k$  value, if no LLS data are supplied, how to scale the absolute value of the MW a polymer and achieve the decided MWD? These all indicate that Tuminello's report about the MWD of ETFE is not convenient in practice.

As a result of those above mentioned, an method for scaling the absolute magnitude of MWD, independent of LLS data, or other external techniques beyond rheometry is needed. Thereby, the Rouse terminal relaxation time theory is introduced into the derivation of the absolute MW of ETFE<sup>3,10,11</sup> and then obtaining the absolute MWD of ETFE via scaling the relative distribution of MW depending on the absolute MW. This scaling method has been validated and more applied, for example, Lavallee and Berker<sup>5</sup> in polystyrene and Zhang et al.<sup>4</sup> in cellulose solution. In a word, this article combines a new scaling MW method with Tuminello's determination of relative MWD via rheology to offer a self-scaling rheology-based MWD characterization technique and gives the absolute and real MWD of commercial ETFE. In our knowledge, this is the first time to characterize MW and MWD of ETFE with completely isolated rheological method.

### Procedure and methodology for deriving MWD via rheology-based technique

Tuminello supposes that the unrelaxed chains within a polymer melt at any frequency ( $\omega_i$ ) are "diluted" by, but not entangled with, the relaxed (lower MW<sub>*i*</sub>) chains. He also postulates that each monodisperse molecular fraction (MW<sub>*i*</sub>) has a single relaxation frequency ( $\omega_i$ ), below which it makes no contribution to the dynamic modulus, thus behaving as a piecewise function. Hence, connecting the cumulative mass fraction of relaxed chains  $C(\text{MW})$  with dynamic modulus can be conducted, namely

$$C(\text{MW}) = 1 - \sqrt{\frac{G'(\omega_i)}{G_N^0}} \quad (1)$$

where  $G'(\omega_i)$  is dynamic storage modulus of polymer fluid, which possesses frequency dependence. In Tuminello's work,  $\sqrt{\frac{G'(\omega_i)}{G_N^0}}$  was referred to as relative

weight fraction of unrelaxed chains and designated as  $Wu$  ( $Wu = \sqrt{\frac{G'(\omega_i)}{G_N^0}}$ ).<sup>9</sup> The derivative of the cumulative  $C(\text{MW})$  is the differential MWD, and so

$$\text{MWD} = \frac{dC(\text{MW})}{d \log(\text{MW})} \quad (2)$$

And the frequency axis is transformed into MW according to the well-known empirical relationship (3).<sup>11</sup>

$$\frac{1}{\omega} = k_1 \eta_0 = k_2 (\text{MW})^{3.4} \quad (3)$$

where  $k_1$  and  $k_2$  are proportionality constants. Incorporating eqs. (1) and (3), the relative MWD can be calculated by<sup>12</sup>

$$\text{MWD} = \frac{dC(\text{MW})}{d \log(\sqrt{1/\omega})} \quad (4)$$

In this above calculation, arbitrary values are used as the proportionality constants, and therefore the results are relative MWD, and thus it is needed to scale the results for obtaining absolute amount of MWD. Tuminello<sup>7</sup> used LLS data to aid calibrating of relative MWD. His handling could insure possibly the accuracy of the results but hurt independency of rheology-based method for the determination of MWD of polymer. In this article, we use the Rouse terminal relaxation time theory to scale the relative MWD. According to the Rouse terminal relaxation time theory,

$$\tau_R = \frac{6\eta_0(\text{MW})}{\pi^2 \rho RT} = \frac{1}{\omega_{\text{ch}}} \quad (5)$$

where  $\tau_R$  is the Rouse terminal relaxation time,  $\rho$  the density,  $\eta_0$  the zero-shear viscosity,  $R$  the universal gas constant,  $T$  the temperature, and  $\tau_R = 1/\omega_{\text{ch}}$ , with  $\omega_{\text{ch}}$  chosen to be the corresponding frequency of the point of maximum curvature of the flow curve.<sup>5</sup> Usually, the frequency associating 79th percentile point of  $\eta_0$  normalized flow curve is seen as  $\omega_{\text{ch}}$  (and could be designated as  $\omega_{79}$ , due to the  $\omega_{79}$  is the transition frequency from Newtonian to non-Newtonian behavior for a polymer fluid, namely at that frequency, the apparent viscosity of the polymer fluid shifts down, and the unentangling is more intensified than the entangling among molecular chains), and therefore based on eq. (5), an ascertained MW can be obtained. In general, the ascertained MW based on  $\omega_{79}$  is believed as the peak MW (Mp).<sup>4</sup> Mp indicates the maximum probability MW on the curve of MWD. Consequently, the peak MW scale is obtained through  $\text{Mp} = \text{MW} = \frac{\pi^2 \rho RT}{6\eta_0 \omega_{79}}$ , and the MWD

scale curve is achieved after shifting the abscissa [ $\log M_p - \log (1/\omega_{79})$ ] amount. Here, the  $M_p$  and  $(1/\omega_{79})$  are the peak MW on the MWD scale curve and relative MWD curve, respectively. Finally, the special weight-average MW ( $M_w$ ) and number-average MW ( $M_n$ ) can be calculated via their definition.<sup>13</sup> Through  $M_w$  and  $M_n$ , polydispersity index (PDI) can be obtained by  $M_w/M_n$ .

The concrete and clear-flow procedure outlined is given in the following part for convenience of understanding the contribution:

- Step 1: measure the dynamic rheological properties of ETFE melt by rotational rheometer and build the master curves of ETFE materials function;
- Step 2: derive the relaxation time spectrum of ETFE and calculate its  $G_N^0$  and  $\eta_0$ ;
- Step 3: use Tuminello nucleus function,  $Tu[\log(\omega)]$  (a hyperbolic tangent function whose independent variable is  $\log(\omega)$ , see also Results and Discussion section), to fit  $Wu$  data and deduce the coefficients of the nucleus function;
- Step 4: calculate  $C(MW)$  and then relative MWD on the basis of the derivative of  $C(MW)$ <sup>†</sup>;
- Step 5: achieve the absolute MWD of ETFE by scaling the maximum probability MW to the peak MW on the relative MWD curve based on Rouse relaxation time theory;
- Step 6: estimate the PDI via Wesslan function.

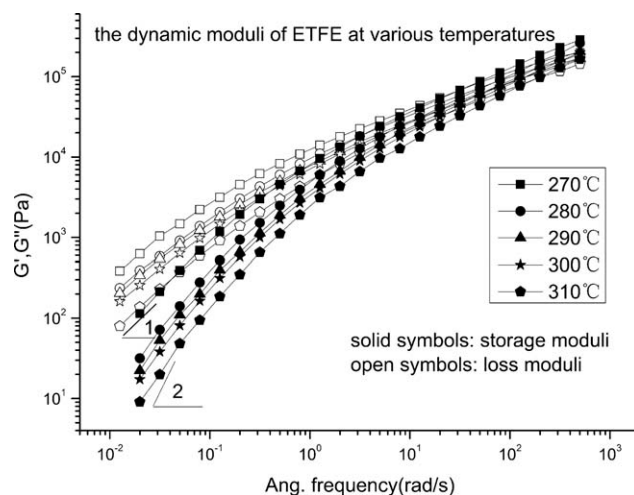
## EXPERIMENTAL

### Materials and sample preparation

The ETFE resin used is EP541 of DaiKin Industries (Japan) and granular form. It possesses melt flow rate of 6 g/10 min (5000 g load and 297°C). After vacuum dried for 2 h at 120°C, ETFE resin granules were forced into the flat sheet sample with the  $100 \times 100 \times 1 \text{ mm}^3$  via a plate vulcanizing machine under 275°C first, and then the sheets were cut into circular pieces with diameter of  $\sim 27 \text{ mm}$  (during the rheological measurements, the circular pieces were cut into specimens with size of  $\Phi 25 \times 1 \text{ mm}$ ).

<sup>†</sup>Its derivation is  $\frac{dC(MW)}{d \log(MW)} = \frac{d(1-Wu)}{d \log(MW)} = \frac{d\{1-Tu[-\log(MW)]\}}{d \log(MW)}$   
 $= Tu'[\log(MW)] = Tu'[-\log(\omega)]$ .

- Where  $Tu'[\log(MW)]$  and  $Tu'[\log(\omega)]$  are the derivative of Tuminello nucleus function, and the independent variables are  $\log(MW)$  and  $\log(\omega)$ , respectively.
- Based on eq. (3),  $\log(MW) \propto \log \frac{1}{\omega}$  can be concluded and then  $\log(\omega) \propto -\log(MW)$ .



**Figure 1** The oscillatory mechanical results of ETFE under various temperatures.

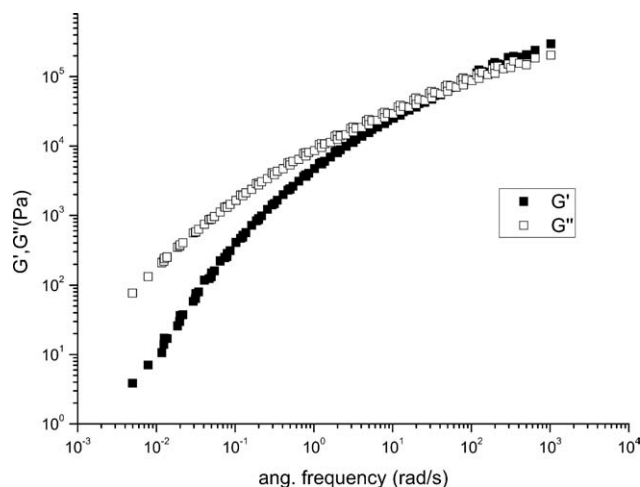
### Rheological measurements

The measurements were performed in AR G2 rheometer (TA Instruments, USA). Parallel geometry, diameter 25 mm, was used. Dynamic frequency sweep experimental was performed within linear viscoelastic zone and nitrogen environment (avoiding oxidation). The frequency range is from 0.01 to 500 rad/s, and the temperatures observed are 270, 280, 290, 300, and 310°C, respectively. In addition, in the low-test temperature cases, a preheating process at 310°C for at least 1 min was conducted to remove the disturbances of residual crystallite in ETFE melt on measurement results. After that process, the sample was cooled down to the desired test temperature and then to oscillatory frequency sweep.

## RESULTS AND DISCUSSION

### The dynamic viscoelastic behavior and calculating viscoelastic parameters ( $G_N^0$ and $\eta_0$ ) involved of ETFE melt

The oscillatory shear measurements can explore viscoelasticity of polymers and investigate hierarchical microstructures existed in their bulk, conveniently and easily. After determining the linear response region by dynamic shear stress sweep, the oscillatory frequency tests were done. Figure 1 shows the dynamic viscoelastic characteristics of five temperatures. It is found that the moduli of ETFE are larger than common polymer such as polyethylene<sup>14</sup> and also behave simply like homogeneous polymers melt, indicating no complex hierarchical motion and relaxation in its molecular chains although its copolymer nature. The so-called terminal region<sup>11,15</sup> has been reached but happens in the very low-frequency zone, which means more difficult molecular motion and relaxation. In the terminal region, the



**Figure 2** The master curves of ETFE at reference temperature of 290°C.

relationship between loss moduli and angular frequencies follows roughly  $G'' \propto \omega$ , namely the scaling coefficient of  $\log G''$  with  $\log \omega$  is near to 1. But the relationship between storage moduli and angular frequencies deviates remarkably from  $G' \propto \omega^2$ , namely in the terminal region, the relationship between  $\log G'$  with  $\log \omega$  is not equal to 2.

In terms of linear viscoelastic theory, thermorheological simple polymer fluids all follow up time-temperature superposition (TTS) and can construct master curve, while master curve can help polymer scholars to obtain very much extra, even total, information on molecular structures, molecular motion, and internal interaction of polymers from finite rheological experimental data. Although a polymer fluid holds thermorheological simplicity if the fluid complies with TTS, practically, before using TTS to achieve master curves of a polymer fluid, the confirmation of thermorheological simplicity, if the fluid has, is done first, such as van Gurp and Palmen's work.<sup>16,17</sup> Here, the simplicity dose not be evaluated but the ETFE melt is thermorheological simple based on the following both facts: (1) the various vertical shift factors during TTS processing are almost unit and (2) the superposition of dynamic moduli under different temperatures is very good, no "shoulder" or spread scattering data happen in the figure (Fig. 2).

The master curves were completed via TA Data Analysis program, a software supported by TA Company. From the master curves, the correspondent Maxwell discrete relaxation time spectrum was calculated. The relaxation time spectrum is the central function of describing mechanical properties and molecular motion and interaction of macromolecules. The relaxation time spectrum can be used to calculate liner material functions from other standard experiments and to cross-check the results with

the predicted behaviors, and it is essential to perform numerical simulations of complex flows of polymeric materials. From the relaxation spectrum, zero shear viscosity and plateau modulus can be derived.<sup>11,14,18</sup>

$$\text{Plateau modulus } G_N^0 = \sum G_i \quad (7)$$

$$\text{Zero shear viscosity } \eta_0 = \sum G_i \lambda_i \quad (8)$$

The discrete Maxwell relaxation time spectrum data are obtained by TA data analysis software package supported by TA Company. Based on the relaxation time spectrum, the plateau modulus of  $4.12 \times 10^5$  Pa and zero-shear viscosity of  $2.49 \times 10^4$  Pa s are attained.

### Calculation of MW scale and the absolute MWD of ETFE

Fit  $Wu$  using Tuminello nucleus function

Tuminello<sup>7,9</sup> fitted with  $Wu$  plot to the following function

$$Tu(x) = Wu = \sqrt{\frac{G'(\omega)}{G_N^0}} = \sum_{i=1}^n \frac{a_i \{1 + \tan H[b_i(x + c_i)]\}}{2} \quad (9)$$

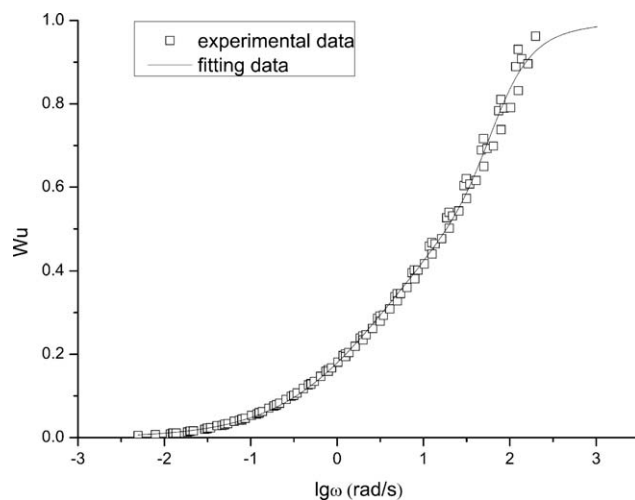
where  $0 < Tu(x) < 1$ ;  $x$  is  $\log \omega$ ;  $\sum a_i = 1$ , controlling the maximum value or the height of each term and  $0 < a_i < 1$ ,  $b_i$  is a parameter adjusting the curve width,  $c_i$  is a parameter that determines the curve on the  $\omega$  axis, and  $n$  is an integer. The optimum value for the integer  $n$  is 2 according to Tuminello's investigation,<sup>7,9</sup> and, thus, here, the integer  $n$  is assigned the value of 2. Because of  $\sum a_i = 1$ , in case of  $n = 2$ ,  $a_2$  will equal to  $1 - a_1$ , and so  $a_i$  parameter is displaced with  $a$  and  $1 - a$ ; therefore, eq. (9) transforms into

$$Tu(x) = Wu = 0.5a\{1 + \tan H[b_1(x + c_1)]\} + 0.5(1 - a)\{1 + \tan H[b_2(x + c_2)]\} \quad (10)$$

$a$ ,  $b_i$ , and  $c_i$  are determined by a numerical software, MATLAB (here, MATLAB R2010a was used). These parameters that we chose from this curve-fitting operation are tabulated in Table I.

**TABLE I**  
Parameters for MATLAB Curve Fits of eq. (10)

Sample	EP541
$a$	0.3289
$B_1$	0.735
$B_2$	0.9843
$C_1$	-6365.0
$C_2$	-5154.2



**Figure 3** Fitting the  $Wu - \log \omega$  curve.

The fitting data and experimental data were plotted in Figure 3. The figure presents that the goodness of fit is very well. The coefficient of determination ( $R^2$ ) between fitting and experimental data is up to 0.9974, and the value of the chi test-statistic ( $\chi^2$ ) is 0.0394.  $R^2$  and  $\chi^2$  provide a measure of how well the fitting outcomes are likely to be predicted by the model, and  $R^2$  nearer to 1 and  $\chi^2$  smaller, the goodness of fit better.<sup>19</sup>

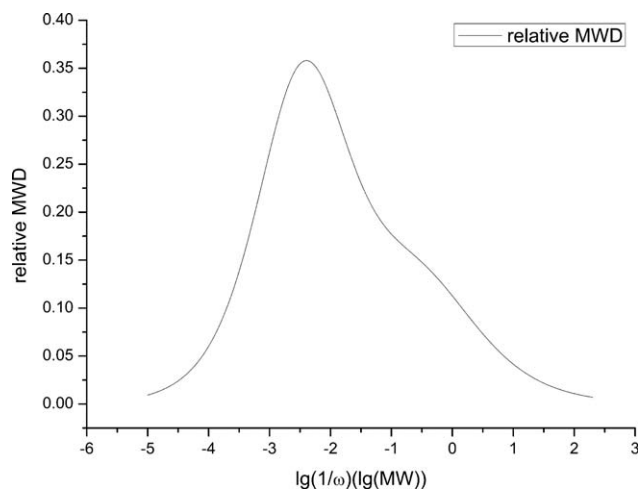
#### Determining the relative MWD

Following the above section, the concrete Tuminello nucleus function expression is obtained, and then in term of the guide of Materials and Methods section, the differential MWD can be achieved from the derivative of  $Wu$ . Applying MATLAB program again, we get the differential MWD whose expression is

$$\text{MWD} = Wu' = 0.5b_2(a-1)\{\tan H[b_2(c_2 - x')]^2 - 1\} + 0.5ab_1\{\tan H[b_1(c_1 - x')]^2 - 1\} \quad (11)$$

where  $x'$  is  $\log MW = \log(1/\omega)$  and  $Wu'$  represents the derivative of  $Wu$  function. After being put the correspondent numerical values in Table I and correspondent  $\log MW$  and  $Wu$  data into the above differential MWD expression, the relative MWD data were attained. This relative MWD curve was plotted in Figure 4.

Figure 4 shows that the MW distribution of ETFE is broad and holds a faint raised "shoulder" on high MW end and a high peak in the median part of the curve. Wide distribution and "high MW shoulder" seem to be abreast of commercial polymer practice due to the need to incorporate exceptional processability into outstanding physical properties decided by high-molecular mass part.



**Figure 4** The relative MWD of ETFE (note: in this figure, the unit of frequency is rad/s).

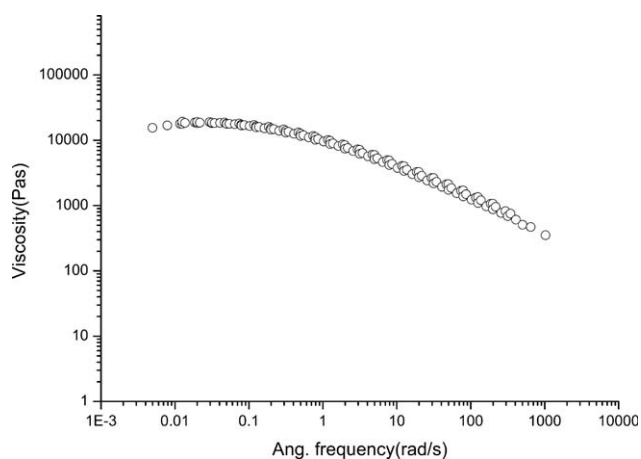
#### Scaling the above relative MWD

For scaling the above relative MWD, the 79th percentile point of zero shear viscosity normalized flow curve is used (Fig. 5 is the not normalized viscosity master curve of ETFE melt at 290°C). The normalized viscosity versus frequency relationship was fitted by Elbirli–Yasuda–Carreau model.<sup>5,20</sup> Elbirli–Yasuda–Carreau model is

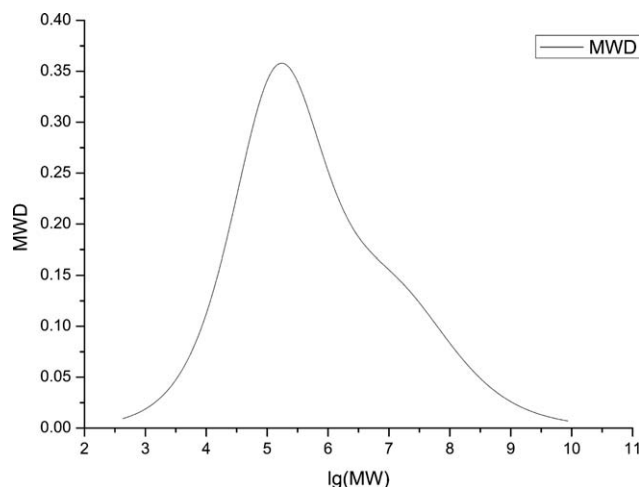
$$\eta = \frac{\eta_0}{[1 + (\lambda\dot{\gamma})^m]^n} \quad (12)$$

By fitting with the aid of MATLAB software package, the three coefficients of eq. (12),  $\lambda$ ,  $m$ , and  $n$ , were gained; therefore,

$$\eta = \frac{24,900}{[1 + (0.1171\omega)^{0.3768}]^{2.4382}} \quad (13)$$



**Figure 5** The viscosity master curve of ETFE melt at 290°C.



**Figure 6** The absolute MWD curve of ETFE (note: in this figure, the unit of frequency is hertz).

At 79th percentile point of zero-shear viscosity normalized flow curve, the correspondent  $\omega_{79}$  is 0.0197 rad/s, viz. 0.0031 Hz, by solving eq. (13). And, thus, on the basis of eq. (5), the Mp of  $1.7348 \times 10^5$  g/mol, also  $\log Mp$  of 5.2392, was obtained, and this Mp value was the peak MW scale on the absolute MWD.

At the same time, with the help of MATLAB software, the derivative of the relative MWD, namely the derivative of differential MWD, was determined. The  $\log(1/\omega_p)$ , in which the derivative of the relative MWD is zero, is  $-2.3940$  by calculation (here, the frequency is angular frequency). And, thus, the absolute MWD curve is obtained by shifting the abscissa [ $\log Mp - \log(1/\omega_p)$ ] distance. The absolute MWD curve is presented in Figure 6.

Through the knowledge of polymer physics, the MW average can be obtained, viz.

$$M_w = \int_0^{\infty} W(M)M dM \quad (14)$$

where  $M_w$  is molecular weight average,  $W(M)$  is weight differential distribution, namely the differential MWD here, and  $M$  is independent variable with the significance of molecular mass. Because calculating calculus of eq. (14) is very difficult, the correspondent MW average has not been given or PDI calculated by sophisticated calculus formula. However, a concrete PDI value is essential for exploring the polydispersity of MW; thus, Wesslan function<sup>13</sup> is adopted to fit the MWD curve of ETFE, and therefore PDI is derived. Wesslan function is expressed as following,

$$y(\ln x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(\ln x - \ln \bar{x}_m)^2}{2\sigma^2}\right) \quad (15)$$

where  $\sigma$  and  $\bar{x}_m$  are coefficients that need to be determined by fitting, while  $y$  is the differential MWD and  $x$  is the MW. Then, the PDI is calculated by eq. (16)

$$\text{PDI} = \exp(\sigma^2) \quad (16)$$

Finally, PDI of ETFE studied here is roughly 10.3. This result is larger than that of Tuminello, and the potential reason may be that the materials of sample are different. It is common sense that different company uses different materials for producing polymer.

## CONCLUSIONS

By assuming the MW of ETFE calculated by the Rouse terminal relaxation time that can be seen as the peak MW on its MWD curves, the reciprocal of frequency was converted absolute MW without use of external technique. This technique has been used successfully in determining MW and MWD of polystyrene and cellulose by other researchers. As a result, the rheology-based method initiated by Tuminello was really used independently, first, in determining MW and MWD of ETFE in our knowledge. The results show that the peak MW of ETFE is  $1.7348 \times 10^5$  g/mol, and the MWD plot is a pattern that possesses a light bump “shoulder” at high-molecular mass end and a high peak on the median part. The PDI was calculated by mean of fitting the MWD curve to Wesslan function, and its amount was up to 10.3. The wide polydispersity signifies that the commodity ETFE, EP541, has better flow ability comparing with ETFE bearing smaller PDI and can incorporate good processability of molecules holding relative lower molecular mass with physical properties of high-molecular mass chains. At last, it is worth noting that the rheological technique is fast and simply in operation, and, thus, our case gives an easy and practical mean to characterize the MW scale and MWD in the production and application of ETFE industry.

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