Polymer Molecular Weight from Loss Modulus

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ABSTRACT: The method for the determination of polymer molecular weight and molecular weight distribution from transient and dynamic viscoelastic properties of a narrow molecular weight distribution linear amorphous polymer with $M_w > M_c$ has been discussed in our previous work. In the present work, we discussed the method to calculate the polymer molecular weight and molecular weight distribution from terminal zone of loss modulus $G''(\omega)$. The terminal zone of loss modulus $G''(\omega)$ is separated from the plateau modulus $G_n{}^0$ and the normalized relaxation time spectrum $H(\tau)$ is then calculated by using the first approximation formulas of Tschoegl. The polymer molecular weight and molecular weight distribution are then obtained from $H(\tau)$ by using the same numerical method as was developed in the previous work. The results calculated by this method are in good agreement with those measured from membrane osmometry, light scattering and GPC experiments etc.
    KEY WORDS   Molecular Weight / Relaxation Spectrum / Loss Modulus /

The viscoelastic property of polymers is closely related to the molecular weight, molecular weight distribution and branches.[1,2] Thus, it plays an essential role in linking polymer structure and processing. Despite the importance of viscoelasticity, a completely good understanding of its relation with molecular weight and molecular weight distribution has been lacking. The dynamic elastic modulus $G'(\omega)$ and transient modulus $G(t)$, in the terminal zone, can be transformed to the cumulative weight fraction as a function of molecular weight.[3,4] In our previous work,[5,6] we have developed a method to determine the molecular weight and molecular weight distribution from terminal zone of storage modulus $G'(\omega)$ and stress relaxation modulus $G(t)$ for a linear amorphous polymer with a molecular weight higher than critical molecular weight M_c. In the present study, we demonstrate another method to determine the linear amorphous polymer molecular weight and molecular weight distribution from terminal zone of loss modulus $G''(\omega)$.

THEORETICAL BACKGROUND

The terminal zone of loss modulus $G''(\omega)$ of a polymer melt contains a spectrum of molecular relaxation times. The relaxation time spectrum is closely related to the polymer molecular weight and molecular weight distribution. The terminal zone of linear viscoelastic dynamic loss modulus $G''(\omega)$ of a polydisperse polymer is given by[1]:

$$G''(\omega) = G_n{}^0 \int_{-\infty}^{\infty} H(\tau) \frac{\omega\tau}{1 + \omega^2\tau^2} \, d\ln\tau \quad (1)$$

where $G''(\omega)$ is the dynamic loss modulus at frequency ω. $H(\tau)$ is the relaxation time spectrum, τ the relaxation time for a monodisperse species is the polydisperse blend,

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and $G_n{}^0$ the plateau modulus.

For a blend of N monodisperse species with the longest relaxation times decreasing from τ_1 to τ_N, each species contributes to the relaxation process of the polydisperse blend through binary contacts. According to Montfort's prediction,[7] the weight contribution to viscoelastic property in the relaxation interval τ_j and τ_{j-1} is equal to the difference between all binaries for $\tau > \tau_j$ and those for $\tau > \tau_{j-1}$, i.e.,

$$\left[\sum_{k=1}^{j} W(\tau_k) \right]^2 - \left[\sum_{i=1}^{j-1} W(\tau_i) \right]^2$$

$$= W(\tau_j) \left[W(\tau_j) + 2 \sum_{k=1}^{j-1} W(\tau_k) \right]$$

$$\cong 2W(\tau_j) \sum_{k=1}^{j} W(\tau_k) \qquad (2)$$

where $W(\tau_j)$ is the weight-fraction of polymer species $-j$. Hence,

$$G''(\omega) = 2G_n{}^0 \sum_{j=1}^{N} W(\tau_j) \sum_{k=1}^{j} W(\tau_k) \frac{\partial \tau_j}{1 + \omega^2 \tau_j{}^2} \qquad (3)$$

$$G''(\omega) = 2G_n{}^0 \int_{0}^{\infty} W(\tau_j) \int_{\tau_j}^{\infty} W(\tau_k) \frac{\omega \tau_j}{1 + \omega^2 \tau_j{}^2}$$

$$\times d\tau_k d\tau_j \qquad (4)$$

let $h(\tau) = W(\tau)\tau$, we obtain

$$G''(\omega) = 2G_n{}^0 \int_{-\infty}^{\infty} h(\tau_j) \int_{\ln \tau_j}^{\infty} h(\tau_k) \frac{\omega \tau_j}{1 + \omega^2 \tau_j{}^2}$$

$$\times d \ln \tau_k \, d \ln \tau_j \qquad (5)$$

Compare eq 1 with eq 5, we obtain the same $H(\tau_j)$ as that we derived from $G(t)$,[5] i.e.,

$$H(\tau_j) = 2h(\tau_j) \int_{\ln \tau_j}^{\infty} h(\tau_k) \, d \ln \tau_k \qquad (6)$$

Since the terminal zone of loss modulus $G''(\omega)$ can be expressed by eq 1, thus the experimental data of $G''(\omega)$ in the terminal zone could be accurately expressed by:

$$G''(\omega) = \frac{G_n{}^0 (\omega \tau_0)^c}{1 + (\omega \tau_0)^{2c}} \qquad (7)$$

In eq 7, τ_0 is the characteristic relaxation time which characterizes the polymer molecular weight. And $0 < c < 1$ is the distribution parameter which characterize the polymer molecular weight distribution. The parameter c decreases as the polymer molecular weight distribution getting broader and c increases as the polymer molecular weight distribution getting narrower. Both τ_0 and c are numerical parameters to be determined, they can be obtained from a nonlinear regression method. τ_0 and c can also be obtained from the maximum of $G''(\omega)$ and the slope of $\log G''(\omega)$ vs. $\log \omega$ in the terminal zone respectively. By taking derivative of $G''(\omega)$ of eq 7 and putting it equal to zero, we obtain

$$\tau_0 = \frac{1}{\omega_m} \qquad (8)$$

where ω_m is the corresponding frequency at the maximum of $G''(\omega)$. Substituting eq 8 into eq 7, we obtain:

$$G''(\omega) = \frac{G_n{}^0 (\omega/\omega_m)^c}{1 + (\omega/\omega_m)^{2c}} \qquad (9)$$

At terminal zone, we may assume that $(\omega/\omega_m)^{2c} \ll 1$. If $\omega < \omega_m/10$, the $(\omega/\omega_m)^{2c}$ term of denominator at right hand side of eq 9 can be neglected. Take logarithm of both side of eq 9, we obtain:

$$\log G''(\omega) = \log G_n{}^0 + c \log(\omega/\omega_m) \qquad (10)$$

for frequency $\omega < \omega_m/10$.

By plotting $\log G''(\omega)$ vs. $\log \omega$ for the corresponding data of frequency $\omega < \omega_m/10$ at terminal zone, c can be obtained from the slope of the plot. Once the parameters c and τ_0 are determined, the normalized relaxation spectrum can be obtained by using the first-order approximation formulas eq 11 and 12 of Tschoegl[8]:

$$H(\tau) = \frac{2}{\pi G_N{}^0} \left[G''(\omega) + \frac{dG''(\omega)}{d \ln \omega} \right] \bigg/ 1/\omega = \sqrt{3}\,\tau \quad (11)$$

for the positive slope of $H(\tau)$ vs. $\ln \tau$, and

$$H(\tau) = \frac{2}{\pi G_N{}^0} \left[G''(\omega) - \frac{dG''(\omega)}{d \ln \omega} \right] \bigg/ 1/\omega = \tau/\sqrt{3} \quad (12)$$

for the negative slope of $H(\tau)$ vs. $\ln \tau$. The calculated value of $H(\tau)$ corresponds to $1/\omega = \sqrt{3}\,\tau$ for positive slope of $H(\tau)$, and $1/\omega = \tau/\sqrt{3}$ for negative slope of $H(\tau)$.

Substituting eq 7 into eq 11 and eq 12, we obtain:

$$H(\tau) = \frac{2}{\pi} \left[\frac{(\omega\tau_0)^c}{1 + (\omega\tau_0)^{2c}} + c\frac{\omega^{c+1}\tau_0{}^{c-1}}{1 + (\omega\tau_0)^{2c}} - \frac{\omega^{3c+1}\tau_0{}^{3c-1}}{[1 + (\omega\tau_0)^{2c}]^2} \right] \quad (13)$$

for positive slope of $H(\tau)$ vs. $\ln \tau$. And,

$$H(\tau) = \frac{2}{\pi} \left[\frac{(\omega\tau_0)^c}{1 + (\omega\tau_0)^{2c}} - c\frac{\omega^{c+1}\tau_0{}^{c-1}}{1 + (\omega\tau_0)^{2c}} + \frac{\omega^{3c+1}\tau_0{}^{3c-1}}{[1 + (\omega\tau_0)^{2c}]^2} \right] \quad (14)$$

for negative slope of $H(\tau)$ vs. $\ln \tau$.

To construct a weight-fraction differential molecular weight distribution curve $W(\tau)$ from $H(\tau)$ by using eq 6, the following computer iteration procedure is used.

(1) The $\ln \tau$ axes of $H(\tau)$ vs. $\ln \tau$ and $h(\tau)$ vs. $\ln \tau$ are divided into N intervals as shown in Figure 1 with the longest relaxation times decreasing from $\ln \tau_1$ to $\ln \tau_N$, and each interval equalling to Δ.

(2) The integration part of eq 6 is calculated by using the trapezoid rule. Suppose the integer N is large, then we may set

$$H(\tau_1) = 2h(\tau_1)\left[\frac{\Delta}{2} h(\tau_1)\right] \quad (15)$$

$$h(\tau_1) = \left[\frac{H(\tau_1)}{\Delta}\right]^{1/2} \quad (16)$$

then

$$W(\tau_1) = h(\tau_1)/\tau_1 \quad (17)$$

let

$$A_1 = \frac{\Delta}{2} H(\tau_1) \quad (18)$$

then

$$H(\tau_2) = 2h(\tau_2)\left[A_1 + \frac{\Delta}{2}(h(\tau_2) + h(\tau_1))\right] \quad (19)$$

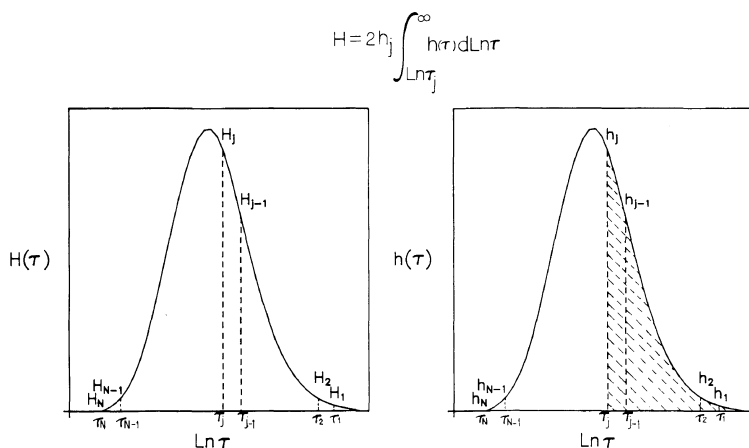$$H = 2h_j \int_{Ln\tau_j}^{\infty} h(\tau)dLn\tau$$

Figure 1. The graph method of the calculation of $h(\tau)$ from eq 6.

$$h(\tau_2) = \frac{1}{2\Delta} [(\Delta h(\tau_1) + 2A_1)^2 + 4\Delta H(\tau_2)]^{1/2}$$

$$- \frac{1}{2\Delta} [\Delta h(\tau_1) + 2A_1] \qquad (20)$$

$$W(\tau_2) = h(\tau_2)/\tau_2 \qquad (21)$$

$$A_2 = A_1 + \frac{\Delta}{2} [h(\tau_1) + h(\tau_2)] \qquad (22)$$

Similarly

$$h(\tau_k) = \frac{1}{2\Delta} [(\Delta h(\tau_{k-1}) + 2A_{k-1})^2 + 4\Delta H(\tau_k)]^{1/2}$$

$$- \frac{1}{2\Delta} [\Delta h(\tau_{k-1}) + 2A_{k-1}] \qquad (23)$$

$$W(\tau_k) = h(\tau_k)/\tau_k \qquad (24)$$

$$A_k = A_{k-1} + \frac{\Delta}{2} [h(\tau_k) + h(\tau_{k-1})] \qquad (25)$$

(3) The relaxation time τ can be converted to the molecular weight scale by using the relation

$$\tau_i = KM_i^a \qquad (26)$$

where $a = 3.4$ for $1 < M_w/M_c < 50$, known empirically, and K can be obtained from the following equation,

$$K = (M_{wr}/M_w)^a \qquad (27)$$

where M_{wr} is the relative weight average molecular weight which will be discussed later, M_w is the weight average molecular weight obtained from other measurements such as gel permeation chromatography (GPC) and light scattering etc. Since

$$\int W(\tau) d\tau = Ka \int W(\tau) M^{a-1} dM = \int W(M) dM \qquad (28)$$

hence,

$$W(M) = KaM^{a-1} W(\tau) \qquad (29)$$

The weight average and number average

molecular weight can be obtained from eq 30 and eq 31 respectively.

$$M_w = \frac{\int W(M)M dM}{\int W(M) dM} = \frac{\int W(M)M^2 d\ln M}{\int W(M)M d\ln M} \qquad (30)$$

$$M_n = \frac{\int W(M) dM}{\int W(M)/M dM} = \frac{\int W(M)M d\ln M}{\int W(M) d\ln M} \qquad (31)$$

In order to calculate M_{wr}, we may set $K = 1$ in eq 26 to calculate the relative molecular weight M_{ir} of polymer species-i with a relaxation time τ_i, the relative weight average molecular weight M_{wr} can then be obtained from eq 30.

APPLICATION TO EXPERIMENTAL DATA

Schausberger et al.[9] measured the loss modulus $G''(\omega)$ of a series of standard polystyrenes of narrow molecular weight distributions. The data were all reduced to a temperature of 180°C. We shall use the data of Schausberger et al. to do data analysis and calculate weight average molecular weight M_w, number average molecular weight M_n and M_w/M_n, and compare the calculated results with those obtained from membrane osmometry, light scattering and gel permeation chromatography.

Table I summarizes the molecular weight data from membrane osmometry, light scattering and GPC which were measured by Schausberger et al.[9]

Figure 2 shows the plot of $\log G''(\omega)$ vs. $\log \omega$ at terminal zone together with the nonlinear least squares fit of eq 7. The plateau modulus G_N^0 which is used in the calculation

Table I. Polystyrene molecular weight data from Schausberger et al.[9a]

Sample	$M_p \times 10^3$	M_w/M_n (GPC)	$M_n \times 10^3$	$M_w \times 10^3$	$M \times 10^3$
PS1	34.5	1.05	33.6	34	39
PS2	61.2	1.06	60.6	—	70
PS3	115	1.05	112	125	128
PS4	260	1.07	271	—	275
PS5	670	1.07	670	750	770
PS6	—	1.05	—	—	3000

[a] M_p, peak of molecular weight distribution of GPC; M_n, molecular weight measured from membrane osmometry; M_w, molecular weight measured from light scattering; M_w/M_n, data measured from GPC; M, molecular weight data provided from manufacture—Polymer Laboratories Ltd.
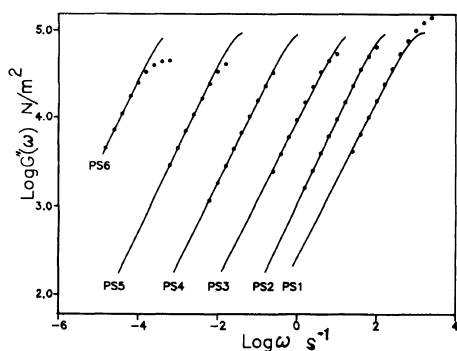

Figure 2. The plot of $\log G''(\omega)$ vs. $\log \omega$ at terminal zone for 6 polystyrene samples. —, theoretical fit of eq 7.

Table II. The parameters τ_0 and c

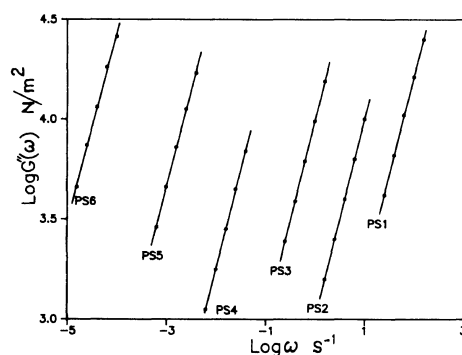| Sample	Eq 7		Eq 8	Eq 10
	τ_0/s	c	$1/\omega_m/s$	c
PS-1	6.23×10^{-4}	0.909	3.98×10^{-4}	0.975
PS-2	4.62×10^{-3}	0.980	6.31×10^{-3}	1.000
PS-3	4.75×10^{-2}	0.991	3.98×10^{-2}	1.000
PS-4	7.81×10^{-1}	0.972	1.00	0.990
PS-5	2.02×10^2	0.968	$2.12 + 10^1$	0.965
PS-6	1.35×10^3	0.970	1.59×10^3	0.995

Figure 3. The plot of $\log G''(\omega)$ vs. $\log \omega$ for $\omega < \omega_m/10$ of 6 polystyrene samples. —, theoretical fit of eq 10.

of nonlinear least squares fit of eq 7 is $10^{5.3}\,N\,m^{-2}$. The plateau modulus $G_N{}^0$ is obtained from $G'(\omega)$ by assuming that $G_N{}^0$ is equal to the corresponding $G'(\omega)$ at which the variation of $\log G'(\omega)$ value vs. $\log \omega$ is minimum.[6] As was shown in the previous work,[6] the plateau modulus $G_N{}^0$ is molecular weight independent. The τ_0 and c for 6 polystyrene samples extracted from the plot of Figure 2 are shown in Table II. Figure 3 is a plot of $\log G''(\omega)$ vs. lof ω of eq 10 for the 6 polystyrene samples together with the linear least squares fit. The parameters τ_0 and c calculated from eq 7, $1/\omega_m$ calculated from eq 8, and c calculated from the plot of eq 10 are listed in Table II.

Figure 4 shows the normalized relaxation spectra $H(\tau)$ of the 6 polystyrene samples calculated from eq 13 and eq 14. The full lines in Figure 4 are the $H(\tau)$ calculated by using the τ_0 and c values obtained from eq 7, and the dashed lines are the $H(\tau)$ calculated by using the τ_0 and c values obtained from eq 8 and eq 10 respectively.

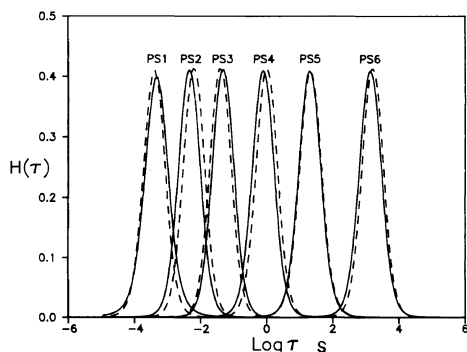Since PS-3 sample has one of the narrowest molecular weight distribution, we use it as a

Figure 4. The normalized relaxation spectra $H(\tau)$ of 6 polystyrene samples calculated from eq 13 and 14. (——) τ_0 and c calculated from eq 7; (– – –) τ_0 and c calculated from eq 8 and 10, respectively.

Figure 5. Plot of $W(M_r)$ vs. $\log M_r$ for sample PS-3. (——) τ_0 and c calculated from eq 7; (– – –) τ_0 and c calculated from eq 8 and 10, respectively.

Figure 6. Plot of $W(M)$ vs. $\log M$ for samples PS-1, PS-2, PS-4, PS-5, and PS-6. (——) τ_0 and c calculated from eq 7; (– – –) τ_0 and c calculated from eq 8 and 10, respectively.

reference sample for the molecular weight calculation. By rearranging eq 26, we obtain

$$M_i = (\tau_i/K)^{1/a} \qquad (32)$$

We put $K=1$ in eq 32 to calculate the relative molecular weight M_{ir} for polymer species-i, the weight fraction of the polymer chain with relaxation time τ_i is computed by using the computer iteration procedure described in the preceding section and the corresponding $W(M_{ir})$ is then calculated from eq 29. Figure 5 shows the weight fraction distribution curve $W(M_r)$ vs. $\log M_r$ for polystyrene sample PS-3, where M_r is the relative molecular weight. The relative weight average molecular weight M_{wr} was then calculated from eq 30. In Figure 5, the full line is the weight fraction distribution curve of PS-3 calculated by using τ_0 and c obtained from eq 7, and the dashed line is the weight fraction distribution curve of PS-3 calculated by using τ_0 and c obtained from eq 8 and eq 10 respectively. The constant "K" can then be obtained from eq 27. Our data analysis of sample PS-3 shows that $M_{wr}=0.52$ and $\log K = -18.294$ for parameters $\tau_0=0.0475$ and $c=0.991$ obtained from eq 7; and $M_{wr}=0.48$ and $\log K = -18.413$ for parameters $\tau_0=0.0398$ and $c=1.00$ obtained from eq 8 and eq 10 respectively.

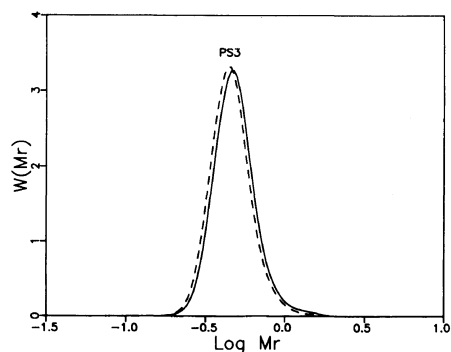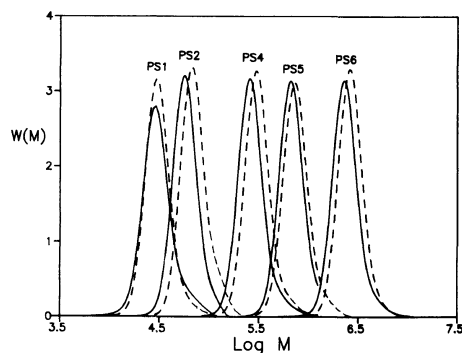Figure 6 is a plot of the weight fraction distribution curves $W(M)$ vs. $\log M$ for polystyrene samples PS-1, PS-2, PS-4, PS-5, and PS-6. In Figure 6, the full lines are weight fraction distribution curves calculated by using τ_0 and c obtained from eq 7, and the dashed lines are the weight fraction distribution curves calculated by using τ_0 and c obtained from eq 8 and eq 10 respectively. The numerical values M_w, M_n and M_w/M_n calculated from the terminal zone of $G''(\omega)$ are also shown in Table III. Good agreement between the results calculated from $G''(\omega)$ and those measured by light scattering, membrane osmometry and GPC are found.

In our previous work, we had calculated the relaxation time spectrum $H(\tau)$ from the

Table III. Polystyrene molecular weight calculated from $G''(\omega)^a$

Sample	From eq 7			From eq 8 and eq 10		
	$M_w \times 10^3$	$M_n \times 10^3$	M_w/M_n	$M_w \times 10^3$	$M_n \times 10^3$	M_w/M_n
PS-1	40.68	31.83	1.28	34.59	29.78	1.16
PS-2	62.83	56.26	1.12	72.43	66.33	1.09
PS-3	Reference	Reference	1.12	Reference	Reference	1.09
PS-4	279.3	254	1.11	323.08	294.89	1.10
PS-5	743.4	664.5	1.12	853.07	734.07	1.16
PS-6	2570	2290	1.12	2854.68	2580.53	1.10

[a] PS-3 reference |eq 7|: $M_{wr}=0.520$; $M_{nr}=0.464$; $\log K = -18.294$. PS-3 reference |eq 8 and eq 11|: $M_{wr}=0.480$; $M_{nr}=0.438$; $\log K = -18.413$.

Table IV. Polystyrene molecular weight calculated from $G'(\omega)^{6\,a}$

Sample	$M_w \times 10^3$	$M_n \times 10^3$	M_w/M_n
PS-1	29.5	27.2	1.08
PS-2	52.8	49.8	1.08
PS-3	Reference	Reference	1.08
PS-4	266	245	1.09
PS-5	692	626	1.10
PS-6	2500	2281	1.09

[a] PS-3 reference: $M_{wr}=0.61$; $M_{nr}=0.56$; $\log K = -18.07$.

terminal zone of storage modulus $G'(\omega)$. The details of the calculating method is described elsewhere.[6] The molecular weight distribution was then calculated from $H(\tau)$ by using the same numerical method as discussed in this paper. Table IV lists the molecular weight and molecular weight distribution data obtained from the terminal zone of storage modulus $G'(\omega)$. Comparing the data shown in Table III and Table IV, we find that the molecular weight and molecular weight distribution calculated from $G'(\omega)$ and $G''(\omega)$ are close.

CONCLUSIONS

In the present work, we demonstrate two methods to estimate the characteristics relaxation time τ_0 and distribution parameter c from the loss modulus $G'(\omega)$. The characteristic relaxation time τ_0 is closely related to the polymer molecular weight and c is related to molecular weight distribution. The parameters τ_0 and c can be obtained either from a nonlinear least squares fit of eq 7 or from the maximum of $G''(\omega)$ and the slope of $\log G''(\omega)$ *vs.* $\log \omega$ in the terminal zone respectively. The first approximation formulas of Tschoegl[8] is then used to calculate $H(\tau)$ in our method, and the polymer MW and molecular weight distribution and then obtained from $H(\tau)$ by using the numerical method we developed in previous work.[5,6]

This method is applicable to linear amorphous polymers with molecular weight $M_w > M_c$. In the present work, we discuss the application of this method to narrow molecular weight distribution polymers. In principle, the relaxation time which governs the relaxation process of a molecule in the flow and rubber transition region is dependent on the length of the molecule and also on the mobility of neighboring molecules. In the blend, the longer molecules behave as if they were shorter than in their own surrounding; and the shorter molecules, as if they were longer. As the molecular weight distribution becomes broader, a shift factor $A_{i,m} = \tau_{i,m}/\tau_i$ (where τ_i is the relaxation time of the component i in its own surrounding; and $\tau_{i,m}$ the relaxation time of the i component in the surrounding which is a mixture of i components with other compo-

nents) should be considered.[10]

For traditional methods such as light scattering, membrane osmometry, and gel permeation chromatography require that a polymer be soluble in a suitable solvent. The advantage for the determination of polymer molecular weight from terminal zone of viscoelastic properties is that we don't need a solvent to dissolve the sample. Hence, this method is suitable for polymers such as fluoro polymers and polyimides etc. which are not able to be dissolved in a solvent.

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