

A Phenomenological Model for Linear Viscoelasticity of Monodisperse Linear Polymers

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Abstract : Although the reptational model of Doi and Edwards gives a successful description of viscoelasticity of flexible linear polymers, the success is restricted to the terminal region.¹ There have been several attempts to modify the Doi-Edwards model to describe wider range of time or frequency.²⁻⁶ This paper suggests a simple phenomenological model which can describe wider range of molecular weight than such molecular models can. Although our model is a phenomenological one, it is practical and convenient to predict the effect of molecular weight distribution on linear viscoelastic data because of its simple mathematical form.

Keywords : monodisperse polymers, linear viscoelasticity, molecular weight.

Introduction

Even in linear region of deformation, most polymers show very complex viscoelastic behavior that prohibits simple modeling with a few parameters. Such complexity may result from molecular weight distribution (MWD) of polymer. Thus, the first step of understanding linear viscoelasticity (LVE) of polymers must be to understand LVE of monodisperse polymers. The second step may be to know the LVE of their mixtures. The last step may be to determine the MWD from LVE of polydisperse polymers.

Before the Doi-Edward (DE) model⁷ appeared, the generalized Maxwell (GM) model seems to have been one of the most efficient way of modeling LVE of polymers. In case of the GM approach, the most interesting theme is to determine or model the relaxation time distribution (RTD). Determination of the RTD from the LVE implies to solve an integral equation, which is known as an ill-posed problem.⁸ Although the GM model gives very accurate curve fitting, it is not a convenient way when one wants to connect LVE with MWD.

The DE theory achieved outstanding success in LVE of polymers. It explains molecular weight dependency of viscoelastic functions. However, the theory is restricted to the

terminal region of entangled polymer melts. In the DE theory, the plateau modulus $G_N^{(0)}$ is independent of molecular weight and is the common scale factor of viscoelastic functions such as the zero shear viscosity η_0 , the steady-state compliance $J_e^{(0)}$ and so on.

There have been several attempts to modify the DE model to fit entire range of LVE. Since all these theories are based on the DE model, the scale factor of the moduli is the plateau modulus that is difficult to be determined when molecular weight is not larger than about ten times of the entanglement molecular weight M_e . This implies that any model scaled by the plateau modulus suffers from difficulty in extension to low molecular weights where the plateau is not clear.

To the knowledge of authors, Lins model² was the first successful modification of the DE model. Although the model was for the relaxation modulus of polymers with very narrow MWD, in curve fitting, it used discrete MWD with 3 peaks, which must be different from a real MWD.

Benallal *et al.*³ developed a molecular model as a simple sum of the reptation and the Rouse modes, contour length fluctuation, and the glassy mode. Although the model describes well the LVE of monodisperse polymers with various molecular weights for wide range of frequency, there is a considerable discrepancy in the loss modulus after the terminal region. Since the model is also based on the DE model, the dynamic and the relaxation moduli are scaled by the plateau modulus.

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Milner and McLeish⁴ did another remarkable molecular modeling, which is also a modification of the DE model. In this model, there is no discrepancy in the loss modulus, different from the model of Benallal *et al.* Furthermore, their approach is applicable to star polymers as well as linear polymers. However, since their model is also a modification of the DE model, the authors did not compare their model with the LVE of the molecular weight range $10M_e > M > M_e$.

Chung and coworkers⁵ also contributed in solving the discrepancy of the original model of Doi and Edwards at high frequency based on slip-link model. Their work is to improve the process X introduced by Lin with more theoretical basis.

Larson and coworkers⁶ did more precise quantitative prediction of LVE for not only monodisperse polymers but also their mixtures. Their approach is a numerical integration of the modified diffusion equation of the reptation. The relaxation modulus is the sum of the Rouse mode from analytical calculation and the reptation mode from the numerical integration. Although their prediction was very precise, all moduli are scaled by the plateau modulus.

In this paper, we aim to develop a simple phenomenological model for monodisperse polymer, which can cover the molecular weight range of $M > M_e$. Its simple mathematical form is efficient in application to the prediction of MWD from LVE of polydisperse polymers.

Theory

The Limit of Molecular Models. The most important success of the DE model is to predict the molecular weight dependence of the zero shear viscosity η_0 for entangled polymer melts. The theory reads⁷

$$\eta_0 = \frac{\pi^2}{12} G_N^{(0)} \tau_d \quad (1)$$

and

$$\tau_d \propto M^{3.4} \quad (2)$$

where $G_N^{(0)}$ is the plateau modulus, τ_d is the disentanglement time and M is molecular weight. Eq. (1) agrees well with experimental data for $M \gg M_e$. The DE theory⁷ explains the LVE of monodisperse polymer by the two characteristic times τ_d and τ_e . The second characteristic time τ_e indicates the start of the plateau of the relaxation or the storage modulus. Since the model assumes the existence of the plateau modulus and uses it as the common scale factor of the zero shear viscosity, dynamic moduli, and the steady-state compliance $J_e^{(0)}$, the model is not valid when the plateau modulus cannot be determined. In other words, this theory cannot be applied to the monodisperse polymers without fully developed entanglement. From the help of the experimental data of Schausbergers *et al.*,¹ one can recognize that the

plateau is not clear when $M < 10M_e$. In order to use LVE of monodisperse polymer for the prediction of those of polydisperse polymers, a candidate model must describe LVE of the monodisperse polymers of $M < 10M_e$.

The Boltzmann superposition principle reads an exact relation between the zero shear viscosity and the relaxation modulus $G(t)$:

$$\eta_0 = \int_0^\infty G(t) dt \quad (3)$$

Figure 1 shows schematic behavior of the relaxation moduli of monodisperse polymers. The area [a] in Figure 1 can be approximated by Eq. (1). When $M > 10M_e$, the plateau can be defined even though the plateau is not perfectly flat. However, when $M < 10M_e$, the two characteristic times τ_d and τ_e are so close that the plateau may not be defined clearly. Thus, when $M < 10M_e$, the integration Eq. (3) cannot be approximated by Eq. (1) because the area [b] in Figure 1 is comparable with the area [a] even though the plateau modulus determined from the LVE of polymers with $M > 10M_e$, is used. Thus, it is necessary to replace the plateau modulus by more generalized scale factor.

The More Generalized Scale Factors of Modulus. To develop a phenomenological model for monodisperse polymers, the experimental data of Schausbergers *et al.*¹ are chosen since they provide tabulated data as well as graphs. They measured LVE of nearly monodisperse polystyrenes with wide range of molecular weights. The reference temperature is 180 °C. Their data are redrawn in Figure 2. The molecular weights of the samples in Figure 2 are shown in Table I.

From the Boltzmann superposition principle, the zero shear viscosity and the steady-state compliance can be obtained from the dynamic moduli⁷:

$$\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''(\omega)}{\omega} \quad (4)$$

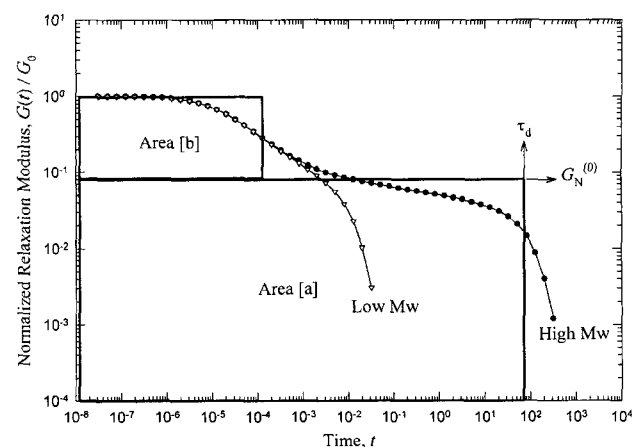


Figure 1. Schematic representation of the relaxation modulus for various molecular weights.

$$\eta_0^2 J_e^{(0)} = \lim_{\omega \rightarrow 0} \frac{G'(\omega)}{\omega^2} \quad (5)$$

Since in the terminal region

$$\begin{aligned} G'(\omega) &\propto \omega^2 \\ G''(\omega) &\propto \omega \end{aligned} \quad (6)$$

it is convenient to define new viscoelastic functions such as

$$\begin{aligned} g'(\omega) &\equiv \frac{G'(\omega)}{\omega^2} \\ g''(\omega) &\equiv \frac{G''(\omega)}{\omega} = \eta'(\omega) \end{aligned} \quad (7)$$

From the Eqs. (4), (5) and (6), it follows that

$$\begin{aligned} \lim_{\omega \rightarrow 0} g'(\omega) &\equiv A_G = J_e^{(0)} \eta_0^2 \\ \lim_{\omega \rightarrow 0} g''(\omega) &= \eta_0 \end{aligned} \quad (8)$$

As shown in Figure 2, the storage and the loss moduli do not have simple forms. However, they have locally power-law type behavior. In Figure 2, one can see that at high frequency, the storage moduli of various molecular weights

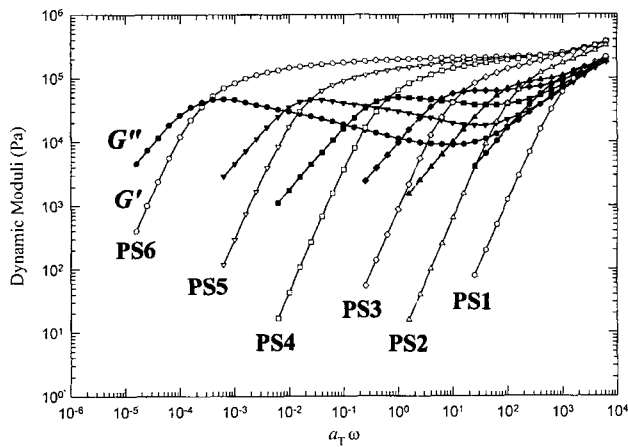


Figure 2. Data of Schausbergers *et al.*¹ The storage (open symbols) and the loss (solid symbols) moduli of polystyrene. The reference temperature is 180 °C. Samples are specified in Table I.

Table I. Data of Molecular Weights (Schausberger *et al.*¹)

Sample	M_w	M_w / M_n
PS1	34,000	1.05
PS2	65,000	1.02
PS3	125,000	1.05
PS4	292,000	1.09
PS5	757,000	1.09
PS6	2,540,000	1.13

look like a single function of frequency. In the terminal region, the dynamic moduli of different molecular weights look like having similar frequency dependency if they are horizontally shifted according to molecular weight. This becomes clearer in the loss modulus. This implies that LVE of monodisperse polymers seems to be, at least, the sum of two functions of frequency. The one represents the reptational mode which can be superposed by a horizontal shifting factor dependent upon molecular weight and the other represents the glassy mode.

If the data of Schausbergers *et al.* are redrawn as the plots of $g'(\omega)/A_G$ and $g''(\omega)/\eta_0$ against $a\omega$ then the plots look like

$$\begin{aligned} \frac{g'(\omega)}{A_G} &\approx \frac{1}{(1+t_d\omega)^p} \\ \frac{g''(\omega)}{\eta_0} &\approx \frac{1}{(1+t_d\omega)^q} \end{aligned} \quad (9)$$

in the terminal region (Figure 3). Since the exponents p and q can be easily obtained as the slopes of the log-log plots, it is not difficult to determine the characteristic time t_d by regression analysis. By the dimensional analysis of η_0 ,

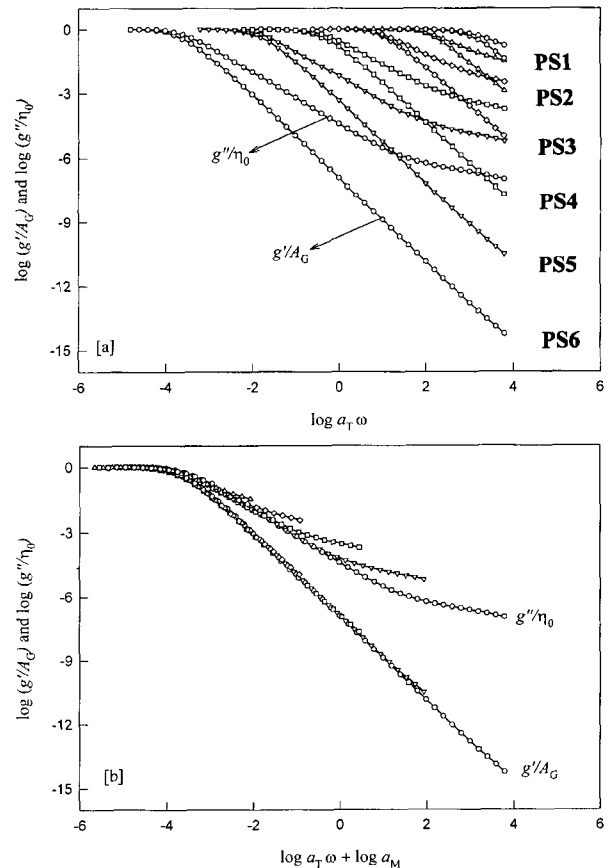


Figure 3. Normalized $g'(\omega)$ and $g''(\omega)$ (a) and their superposition by molecular weight shifting factor a_M (b).

A_G , and t_d , one can define two moduli which can be used as the scale factors for the dynamic moduli instead of the plateau modulus:

$$\begin{aligned} G_0' &\equiv \frac{A_G}{t_d^2} \\ G_0'' &= \frac{\eta_0}{t_d} \end{aligned} \quad (10)$$

From the help of Eqs. (4) and (5), we have

$$G_0' = J_e^{(0)} G_0''^2 \quad (11)$$

Since the terminal behavior Eq. (6) is clear for any molecular weight, the scale factors for modulus, G_0' and G_0'' can be determined from any experimental result irrespective of molecular weight. Thus, the new scale factors G_0' and G_0'' are more generalized than the plateau modulus $G_N^{(0)}$ in this respect.

The shapes of $g'(\omega)/A_G$ and $g''(\omega)/\eta_0$ in Figure 3(a) are almost independent of molecular weight and they can be superposed by a horizontal shift factor. Figure 3(b) is a superposed version of Figure 3(a) where data are horizontally shifted until data of the terminal region are coincided. The superposition of Figure 3(a) makes it clearer that the dynamic moduli are the sum of the two functions, called the reptational and the glassy modes. The branching of $g''(\omega)/\eta_0$ at higher frequency corresponds to the glassy mode.

The glassy modes of different molecular weights in Figure 3 look like an identical form if they are shifted by an appropriate vertical shifting factor, which is dependent upon molecular weight. This implies that there is another scale factor of modulus for the glassy mode, say G_g . Thus, we suggest mathematical forms of the dynamic modulus as follows:

$$\begin{aligned} G'(\omega) &= G_0' \frac{t_d^2 \omega^2}{(1+t_d \omega)^p} + G_g f'(\omega) \\ G''(\omega) &= G_0'' \frac{t_d \omega}{(1+t_d \omega)^q} + G_g f''(\omega) \end{aligned} \quad (12)$$

where G_0' , G_0'' , and G_g are the new generalized scale factors which are dependent on molecular weight, and $f'(\omega)$ and $f''(\omega)$ are functions of frequency to be determined by experimental data. Of course, $f'(\omega)$ and $f''(\omega)$ are independent of molecular weight, since they represent the glassy mode and all molecular weight dependency are concentrated on G_g .

The Characteristic Times. At long time scale or in molten state, the main stress contribution originates from the entropy change of chain conformation. However, at short time scale or in glassy state, the main contribution of stress

results from interaction energy of the segments in polymer chains. Thus, it is a reasonable viewpoint that there are two relaxation modes according to the origin of stress. One is the relaxation of the entropic stress that may be expressed by the gradient of the conformational entropy with respect to an appropriate strain measure. The other is the relaxation of the energetic stress, called the glassy mode. The former represents the long spatial-range interaction by topological constraints and the latter the short spatial-range interaction between the segments, which includes the intramolecular and the intermolecular interactions.

Thus, from above reasoning, one may think that there are two characteristic time scales for each relaxation mode. The first characteristic time can be chosen as t_d which is a function of molecular weight and temperature. It must depend on the reptational diffusion length $L(M,T)$ and the reptational diffusion coefficient $D(M,T)$:

$$t_d = \frac{L^2}{D} \quad (13)$$

The second characteristic time t_0 must be independent of molecular weight since it represents the short-range interaction. It must be a function of parameters of the segments such as monomeric friction coefficient and the size of the segments.

Assuming the time temperature superposition (TTS), the two characteristic time scales must have the same temperature dependence, called the temperature horizontal shift factor a_T . Since the experimental data in Figures 2 and 3 show that both the reptational and the glassy modes of different molecular weights have very similar shape except that the reptational mode is horizontally shifted by molecular weight, it is reasonable assumption that the reptational characteristic time t_d consists of two horizontal shift factors a_T and a_M :

$$\begin{aligned} t_d &= t_d^{ref} a_M a_T \\ t_0 &= t_0^{ref} a_T \end{aligned} \quad (14)$$

The molecular weight dependency of a_M can be determined from experimental data which are shown in Figure 4. In order to guarantee TTS, Eq. (12) must be

$$\begin{aligned} G'(\omega) &= G_0' \frac{t_d^2 \omega^2}{(1+t_d \omega)^p} + G_g f'(t_0 \omega) \\ G''(\omega) &= G_0'' \frac{t_d \omega}{(1+t_d \omega)^q} + G_g f''(t_0 \omega) \end{aligned} \quad (15)$$

The characteristic time t_0 determines the location of the functions f' and f'' in the plots of the dynamic moduli versus frequency.

The Model. Finally, we suggest following model for the dynamic moduli of monodisperse polymers:

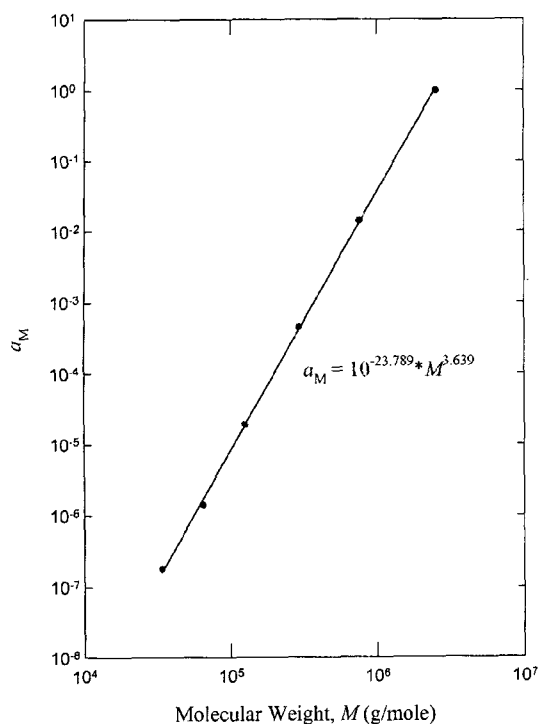


Figure 4. The molecular weight shifting factor a_M as a function of molecular weight.

$$G'(\omega, T) = G_0' \frac{(t_d \omega)^2}{(1 + t_d \omega)^p} + G_g \frac{(t_0 \omega)^m}{1 + (t_0 \omega)^m} \quad (16)$$

$$G''(\omega, T) = G_0'' \frac{t_d \omega}{(1 + t_d \omega)^q} + G_g \frac{(t_0 \omega)^n}{1 + (t_0 \omega)^m}$$

The molecular weight dependency of G_0' and G_0'' can be determined by the slopes of the dynamic moduli in the terminal region, A_G and η_0 respectively. Figure 5 shows molecular weight dependencies of A_G and η_0 . Figure 6 shows the molecular weight dependency of G_0' and G_0'' when the reference time t_d^{ref} was chosen as the reptational characteristic time of PS6 ($t_d^{ref} = 3965$ sec). Since the nature of G_0' and G_0'' is very similar to that of the plateau modulus, G_0' and G_0'' become constant as molecular weight increases. On the other hand, both of them increase as molecular weight decreases. Such molecular weight dependency is the same as that of the inverse of the steady-state compliance $J_e^{(0)}$.^{7,9} Experimental data of Figure 6 are fitted well by following equations:

$$G_0' = C_0' + \frac{C_1'}{1 + M/M_c} \quad (17)$$

$$G_0'' = C_0'' + \frac{C_1''}{1 + M/M_c}$$

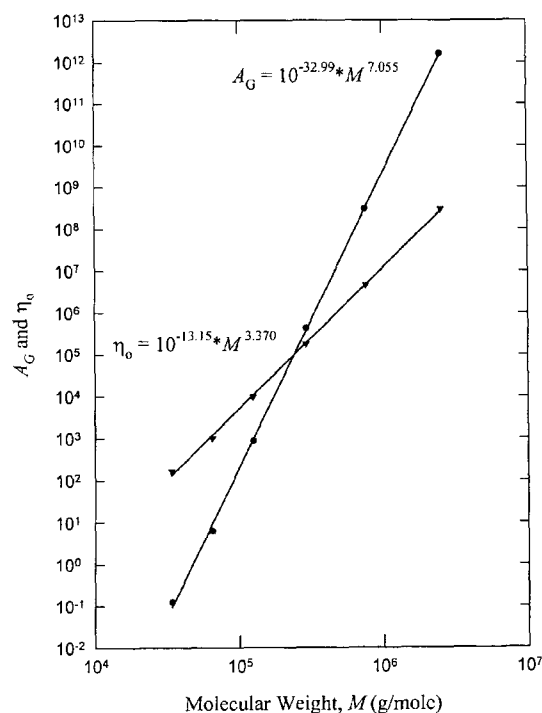


Figure 5. Molecular weight dependency of the zero shear viscosity and A_G .

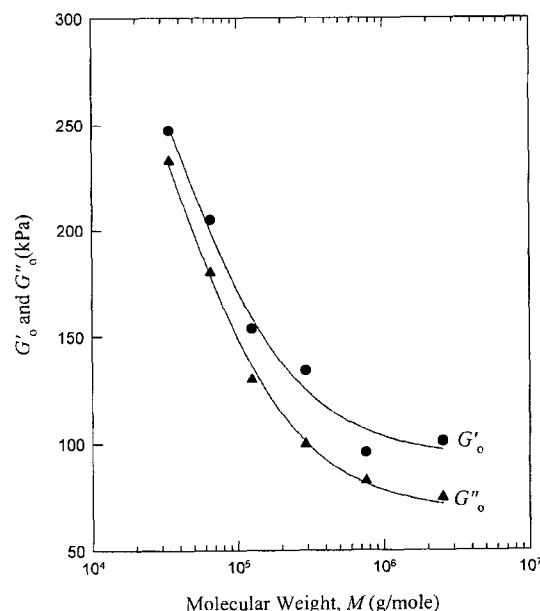


Figure 6. The modulus scale factors for the reptational mode, G_0' and G_0'' as functions of molecular weight.

where C_0', C_1', C_0'' , and C_1'' are material constant with dimension of modulus and M_c is a critical molecular weight.

Differently from G_0' and G_0'' , experimental data are not sufficient to describe molecular weight dependency of G_2 .

However, most physical properties of polymers increase as molecular weight until certain critical molecular weight and after the critical molecular weight, the physical properties are nearly constant.¹⁰ Such molecular weight dependency may be approximated by

$$G_s = \frac{G_\infty}{1 + M_c/M} \quad (18)$$

where G_∞ is the glassy modulus at infinite molecular weight, M_c is chosen as the same molecular weight in Eq. (17).

Results and Discussion

To obtain the data of Figure 6, t_d was determined by non-linear regression and superposition of Figure 3. The shift factor a_M as a function of molecular weight is shown in Figure 4. The regression of a_M with respect to M results in

$$a_M = 10^{-23.276} M^{3.639} \quad (19)$$

Although this result shows that t_d is not proportional to $M^{3.4 \pm 0.1}$, the zero shear viscosity determined from G'' shows (Figure 5)

$$\eta_0 = 10^{-13.75} M^{3.370} \quad (20)$$

The regression results Eqs. (19) and (20) are not surprising, because for wide range of molecular weight, the zero shear viscosity is no longer product of the plateau modulus and the maximum relaxation time τ_d . In addition, it is difficult to determine the plateau modulus. As shown in Lins experimental data,² the log-log plot of the relaxation modulus versus time, there is a significant slope in the plateau region. Thus the plateau modulus is not well-defined quantity from experimental data compared with G'_0 and G''_0 .

Determination of the parameters of the glassy mode, t_0 , m , n , and G_∞ requires data of higher frequency which are not easily found in literatures. Thus, we consider the parameters of the glassy mode as adjustable parameters. To reduce the number of parameters, a critical molecular weight M_c is chosen as about two times of M_e , $M_c = 32,000$ g/mole.

The parameters of curve fitting for the data of Schaus-

Table II. Parameters for Curve Fitting

p	1.93	G_∞	7×10^7 Pa
q	1.25	G'_0	9.3×10^4 Pa
m	1.62	G'_1	3.2×10^5 Pa
n	0.62	G''_0	6.7×10^4 Pa
t_d^{ref}	3965 sec	G''_1	3.4×10^5 Pa
t_0	10^{-8} sec	M_c	32,000 g/mole

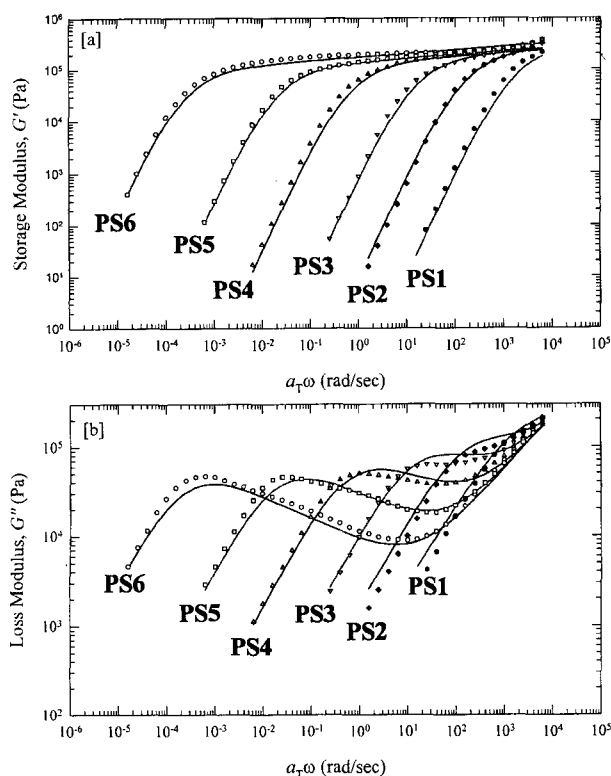


Figure 7. Comparison of the model with the experimental data of Schausbergers *et al.*¹ (a) The storage modulus and (b) the loss modulus.

bergers *et al.* also are shown in Table II. Usually, all molecular models mentioned above fitted only 3 polystyrene of Schausbergers *et al.*, PS4, PS5, and PS6, whose molecular weights are larger than $10 M_e$. It is because the plateau region is well defined for such polymer samples.

Figure 7 shows the curve fitting of the model for the data of Schausbergers *et al.* The model agrees well with all samples of Schausbergers *et al.* Thus, the model is expected to be efficient in application to the prediction of MWD from LVE since it gives good curve fitting for wider range of molecular weight with simple mathematical form.

Conclusions

We develop a phenomenological model for LVE of linear monodisperse polymers, which gives good curve fitting for wider range of molecular weight with simpler mathematical form than the previous molecular models. Instead of the plateau modulus, the model is based on three scale factors of modulus, which are well-defined from experimental data.

The LVE of monodisperse polymer can be described by the sum of two contribution, the reptational and the glassy modes, whose characteristic time scales are t_d and t_0 . It is expected that the simple phenomenological model is more efficient in the prediction of MWD from LVE than the

molecular models.

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