Modeling of the Transient Viscosity for Polymer Melts after Startup of Shearing and Elongational Deformations

Yongsok Seo

Supercomputational Modeling and Simulation Laboratory, Future Technology Research Division, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul, South Korea

Received 10 January 2002; accepted 20 May 2002

ABSTRACT: In order to describe the transient stress growth for polymer melts, the empirical model proposed by Seo for the viscosity of steady-state flow is combined with a phenomenological viscoelastic model of a differential type (the White–Metzner model) along the lines proposed by Souvaliotis and Beris. The relaxation time is taken as a function of the invariant of the stress tensor (hence that of the configuration tensor) rather than that of the rate of the deformation tensor. Numerical results show a good correlation with experimental data. The model predictions approach steady-state values at long times after the startup. The nonlinear form of the model correlates very well with the experimental data over many decades of the deformation rate, both in shearing and elongational deformations. The proposed model is a simple one that can also describe the overshoot in the transient stress growth. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 510–515, 2003

Key words: modeling; transient viscosity; shear flow; elongational flow; viscoelastic model

INTRODUCTION

As is well known, the description of viscoelastic materials essentially depends on the choice of a constitutive model, and no single choice of constitutive equation will be best for all purposes.[1,2] The ultimate success of a constitutive equation rests on its ability to describe the experimental data over a wide range of flows.

Motivated by Graessley's entanglement network theory, we proposed a few years ago a simple nonlinear model that successfully described the steady-state viscosity in shear flow for diverse polymer melts and solutions[3,4]:

$$\log(\eta) = m_1 \tan^{-1}[m_2 - \log(\lambda_e \dot{\gamma})] + m_3 \qquad (1a)$$

or

$$\log(\eta) = m_1 \tan^{-1}[m_2' - \log(\dot{\gamma})] + m_3 \qquad (1b)$$

where $\dot{\gamma}$ is the shear rate, m_1, m_2 (or m_2'), and m_3 are fitting parameters, and λ_e is a time constant like the relaxation time of the polymer. After being combined with Wagner's relationship,[5] our model could predict the first normal stress coefficient, and the prediction correlated very well with the experimental data over many decades of the shear rate.[3] By adopting the White–Metzner model (WM),[6] the proposed model was also successfully applied to elongational flow behavior.[3] The expression for the extensional viscosity can be written as[7,8]

$$\eta_E = 2\eta_s(\mathrm{II}_D)\Big/\left[1 - \frac{2}{\sqrt{3}}\lambda(\mathrm{II}_D)\mathrm{II}_D\right] + \eta_S(\mathrm{II}_D)\Big/\left[1 + \frac{1}{\sqrt{3}}\lambda(\mathrm{II}_D)\mathrm{II}_D\right] \qquad (2)$$

where η_s is the viscosity that depends on the deformation rate obtained from eq. (1) and II_D is the second invariant of the deformation tensor. To account for the fact that high strain rates reduce the relaxation time, we applied the following equation for the relaxation time proposed by Ide and White[8]:

$$\lambda(\mathrm{II}_D) = \lambda_0/(1 + K\mathrm{II}_D) \qquad (3)$$

where λ_0 and K are parameters with the dimensions of time. The proposed model describes both the extensional-flow and the shearing-flow behaviors in the steady state very well.[3]

Though the model successfully described the steady-state shear and elongational behaviors of polymer melts and solutions, it could not depict the stress growth function in shear and elongational deformations because the WM model's expression for the transient viscosity monotonically approaches a steady-state value.[2] Actually, all convected Jeffrey models, including the WM model, follow this trend.[2] This is

Correspondence to: Y. Seo (ysseo@kist.re.kr).

Contract grant sponsor: Korea Institute of Science and Technology; contract grant number: 2E17421.

Journal of Applied Polymer Science, Vol. 88, 510–515 (2003)

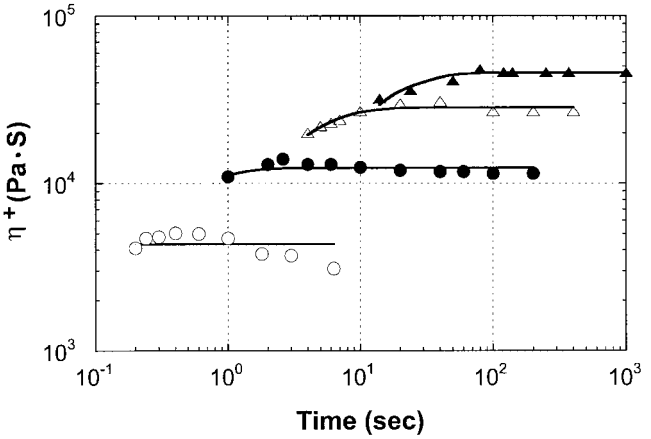

Figure 1 Comparison of the transient viscosity after startup of shearing motion in a low-density polyethylene (LDPE I) melt with the predictions of the White–Metzner model. Shear rate $\dot{\gamma}$ = (filled triangle) 0.01 s^{-1}, (open triangle) 0.1 s^{-1}, (filled circle) 1 s^{-1}, (open circle) 10 s^{-1}. Data of Laun.[13,14]

ascribed to the loss of evolution caused by the direct dependence of the model on the deformation rate.[9–11]

The shear viscosity for the startup of shear flow (η^+) is represented in the WM model as

$$\eta^+(t,\dot{\gamma}) = \eta(\dot{\gamma})[1 - \exp\{-t/[\lambda(\dot{\gamma})]\}] \qquad (4)$$

Figure 1 shows a correlation of the numerical results of eq. (4) with the experimental data. The model cannot describe the stress overshoot.[2] Souvaliotis and Beris[12] pointed out that a number of the problems with the WM model are caused by the direct dependence of its parameters on the deformation rate. Following White–Metzner's original statement,[6] they noted that the relaxation time should be a function of the invariants of the stress matrix. This idea of a phenomenological modification of the upper convected Maxwell model being based on the invariants of the configuration tensor (hence on those of the stress tensor) rather than on those of the rate of strain tensor arises naturally with the context of generalized bracket formulation, which provides the thermodynamic admissibility of any proposed viscoelastic constitutive model.[12] Adopting a power-law dependence of the relaxation time and the viscosity on the trace of the configurational tensorial internal parameter, they got reasonable predictions, including a finite zero-shear-rate viscosity and nonsingular behavior in extension flow.[12] A multiple-mode version was used in fitting the experimental data. Depending on the values of the parameters, reasonable agreement with steady-state shear experimental data could be obtained, while prediction of the transient viscosity at the startup of shear flow was rather unsatisfactory.[12] Although the modified model showed a slight overshoot, it underpredicted the actual overshoot. Also, the theoretical predictions based on the values of the parameters obtained from the steady-state shear normal stress data failed to predict the steady-state values of the viscosity.

In this study, we follow the Souvaliotis and Beris[12] idea that the relaxation time is a function of the invariants of the configuration tensor (hence those of the stress matrix). However, we use the same functional form for the viscosity function as what was used for the steady-state viscosity function. By doing this, we can use the original idea of White–Metzner with respect to the relaxation time. This approach is similar to the so-called time–strain separability, that is, the stress tensor is factored into a time-dependent part and a strain-dependent part.[1] The dependence of relaxation time on the invariants of the configuration tensor will change the behavior of the results predicted by the model.

MODEL DESCRIPTION

Equation (4) was derived from the convected Jeffrey's model.[2] If the relaxation time is a function of the trace of the stress tensor (hence that of the configurational tensor), Jeffrey's model cannot be directly integrated. We must resort to the numerical analysis to get the corresponding stress tensor. Then, optimization of the variables by fitting the experimental data needs a recursive iteration. First, the steady-state solution was used to get the starting values. The steady-state viscosity function of eq. (1) was used for the initial calculation.

The WM constitutive model is usually presented in the following form:

$$\tau + \lambda(\dot{\gamma})\tau_{(1)} = 2\eta(\dot{\gamma})\mathbf{D} \qquad (5)$$

where τ is the extra stress tensor, $\tau_{(1)}$ is its upper convected derivative, $\mathbf{D}$ is the rate of the deformation tensor, $\dot{\gamma}$ is the second invariant of the rate of the strain tensor, and $\lambda(\dot{\gamma})$ is the relaxation time.[1,2]

For the relaxation time, we used a simple functional form similar to one proposed by Ide and White.[8] However, our relaxation time was a function of the first invariant of the stress tensor, σ, rather than a function of the second invariant of the rate of the deformation tensor, that is,

$$\lambda = \frac{\lambda_0}{1 + K\lambda_0[\mathrm{tr}(\sigma)]} \qquad (6)$$

where $\mathrm{tr}(\sigma)$ is the trace of the stress tensor, σ, which is

$$\mathrm{tr}(\sigma) = \mathrm{tr}(\tau) + 3G_0 \qquad (7)$$

and G_0 is the modulus of elasticity. The value of the startup steady-shear flow was used as the initial value of the extra stress tensor[2]:

$$\mathrm{tr}(\tau) = 2\eta_0(\dot{\gamma}_0)\dot{\gamma}_0^2\lambda[1 - (1 + t/\lambda)e^{-t/\lambda}] \quad (8)$$

The numerical solution procedure was as follows. First, the steady-state viscosity function was fitted with the experimental data by using eq. (1). Then, the invariant of the stress tensor was calculated using eq. (8), and the relaxation time was obtained from the calculated invariant and from eq. (6) with initial guess of λ_0 and K values. Using the relaxation time as a function of the invariant, the transient shear viscosity for the startup of shear flow was fitted. From this regressional fitting, a new relaxation time was obtained and then used to calculate the invariant of the stress tensor again. This procedure was repeated until a reasonable convergence was obtained in the parameter values (λ_0 and K). After that, the same procedure was repeated for the whole data to get a series of relaxation times.

The same strategy was used for the calculation of the transient elongational viscosity, $\eta_E{}^+$, after startup of elongational flow. In the WM model, the viscosity of the steady shear free flow is[2]

$$\eta_E^+ = \frac{2\eta_{E0}(\dot{\varepsilon})}{(1 - 2\lambda\dot{\varepsilon})}[1 - e^{-(1-2\lambda\dot{\varepsilon})t/\lambda}] + \frac{\eta_{E0}(\dot{\varepsilon})}{(1 + \lambda\dot{\varepsilon})}[1 - e^{-(1+\lambda\dot{\varepsilon})t/\lambda}] \quad (9)$$

where $\dot{\epsilon}$ is the elongation rate. Then, $\mathrm{tr}(\sigma) = \mathrm{tr}(\tau) + 3G_0$, where

$$\mathrm{tr}(\tau) = \frac{2\eta_{E0}(\dot{\varepsilon})\dot{\varepsilon}}{(1 + \lambda\dot{\varepsilon})}[1 - e^{-(1+\lambda\dot{\varepsilon})t/\lambda}] - \frac{2\eta_{E0}(\dot{\varepsilon})\dot{\varepsilon}}{(1 - 2\lambda\dot{\varepsilon})}[1 - e^{-(1-2\lambda\dot{\varepsilon})t/\lambda}] \quad (10)$$

The calculation procedure was the same as that given above; first, the steady-state elongational viscosity [$\eta_{E0}(\dot{\epsilon})$] values were fitted using the same shear viscosity functional form to calculate the trace of the stress tensor for different elongation ratios.[3] Then, the invariant of the stress tensor was calculated using eq. (10), and a new relaxation time was obtained with the calculated invariant data. Using the new relaxation time as a function of the invariant, the transient elongational viscosity for the startup of transient elongational flow was fitted. From this regressional fitting, a new relaxation time was obtained and then was used to calculate the invariant of the stress tensor again. This procedure was repeated until a reasonable convergence was obtained in the parameter values (λ_0 and K). After that, the same procedure was repeated for the whole data to get a series of relaxation times.

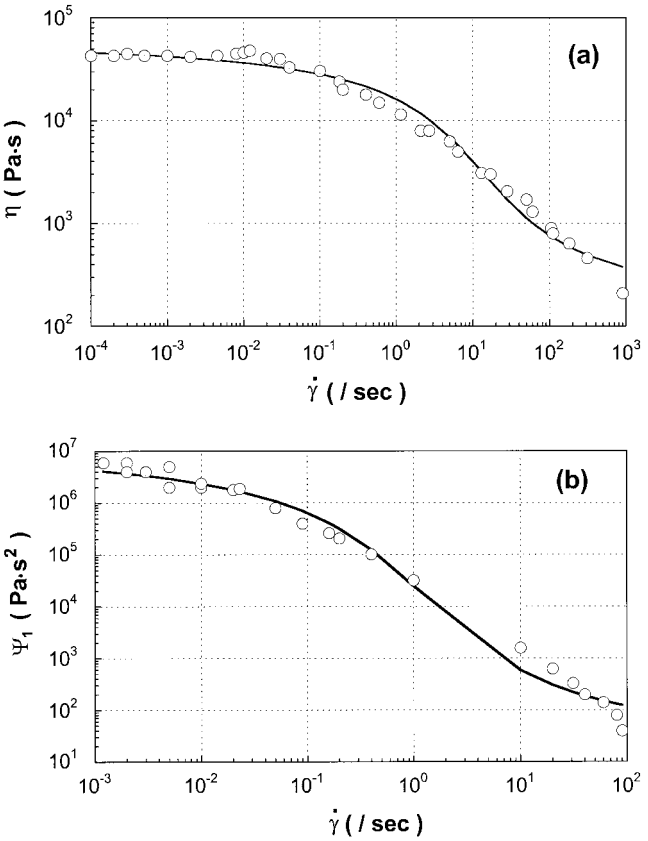

Figure 2 (a) Viscosity function η of the LDPE I melt. The values were calculated by eq. (1b) ($m_1 = 0.852$, $m'_2 = 1.137$, $m_3 = 3.488$). (b) Comparison of the first normal stress coefficient, Ψ_1, of the LDPE I melt with the predictions of eq. (11). The value of n was 0.18 (from Seo[3]).

RESULTS AND DISCUSSION

In order to see how the model works, we compared the results of the calculation with the experimental data reported in the literature for low-density polyethylene (LDPE I). This polymer melt has been extensively studied by Laun[13,14] and Meissner.[15–17] Information on the relaxation spectrum of this melt at 150°C is given by Laun,[13,14] but we attempted first to fit the data with the single relaxation time model of eq. (4). Even though a fitting based on the superposition of discrete modes can be successful in homogeneous flows, it is certainly impractical in numerical simulations.

In our previous study,[3] the experimentally measured zero-shear-rate viscosity and the first normal stress coefficient were correlated with the model prediction using eq. (1) (Fig. 2). Though eq. (1) represents only a three-parameter model, the predictions of its nonlinear form correlate well with the data for very polydisperse LDPE I in spite of the very wide varia-

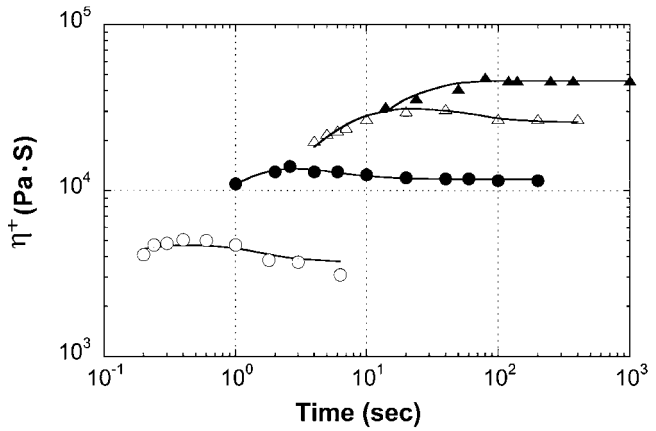

Figure 3 Comparison of the transient viscosity after startup of the shearing motion for an LDPE I melt with the predictions of the present model. Shear rate $\dot{\gamma}$ = (filled triangle) 0.01 s^{-1}, (open triangle) 0.1 s^{-1}, (filled circle) 1 s^{-1}, (open circle) 10 s^{-1}. Data of Laun.[13,14] The same viscosity function as in Figure 2 was used.

tion of viscosity. For the prediction of the first normal stress function, Wagner's relationship[5] was used:

$$\Psi_1 = -\frac{1}{n}\frac{d\eta}{d\dot{\gamma}} \tag{11}$$

where Ψ_1 is the first normal stress function and η is the shear viscosity function obtained from eq. (1). This relationship results from a K-BKZ–type single-integral constitutive equation. The material parameter n (damping constant) is associated with the strain dependence of the memory function. The agreement between the experimental data and the model prediction is quite good, as shown in Figure 2. Souvaliotis and Beris[12] had to use different parameter values to achieve the best fits of Ψ_1 and η, but we used the same parameter values (m_1, m_2, and m_3) for both functions.

Figure 3 shows the transient viscosity η^+ after startup of the shearing motion for the LDPE I melt. Souvaliotis and Beris[12] used an extended WM model with multiple relaxation time mode, but the theoretical prediction underpredicted the actual overshoot. Here we used four relaxation time modes, similar to a discrete linear viscoelastic relaxation spectrum.[13,14] The present model matches the experimental data quite satisfactorily. The optimized time–parameter value (λ_0) decreases rapidly with the shear rate, whereas K shows the opposite trend (Table I). These behaviors are similar to those of other predictions.[12] This result corroborates the idea of the original WM model and the one extended by Souvaliotis and Beris[12] that a generalized bracket formulation where the relaxation time is defined as a function of an invariant of the configuration tensor (hence that of the stress tensor) leads to more satisfying agreement with real phenomena. This is ascribed to the model that keeps its evolutionarity and satisfies the entropy production inequality.[11,12] Because of the inherent properties of the inverse tangent function in eq. (1), the linear viscoelasticity for small deformations can be kept. Its derivative for eq. (1) has the same form as the corotated Maxwell model.[1] Though the current model keeps the viscosity as a function of the second invariant of the rate of the deformation tensor, changing the relaxation time to a function of the first invariant of the stress tensor produces the correct prediction. By the same token, the second invariant of the stress tensor can also be used for the relaxation time function, but as verified by Takahashi et al.,[18] the equation in which the first invariant of the stress tensor is used gives much better agreement with the experimental data than the equation in which the second invariant is included. In some cases, a numerical unstability occurred during the iteration. We are not sure yet if that happened because the invariant of the rate of the deformation tensor was used for the viscosity function rather than the invariant of the stress tensor. This merits further study in the future.

The predictions of the current model are compared in Figure 4 to the data obtained for the startup of elongational motion. The values of η_E from eq. (3) were used for $\eta_{E0}(\dot{\epsilon})$ in eq. (8). Using the same four relaxation time modes as that used for the shearing motion did not give us satisfying results. We had to use more discrete relaxation times. This is similar to other observation. Souvaliotis and Beris[12] as well as Khan and Larson[21] had to use different parameter values fitting for transient shear viscosity and transient elongational viscosity. When more discrete relaxation times were used (Table II), good agreement over a wide range of deformation rates and times was observed. As the elongation rate decreases, the time constant increases rapidly except when the elongation rate is very small, in which case an almost steady state is reached. According to eq. (8), a small relaxation time constant and a small elongation rate have almost a negligible effect on the variation of the transient elongational viscosity with time, which is in agreement with the experimental data. As we mentioned before, the inverse tangent function in eq. (1) approaches the linear viscoelasticity in low deformation rate. The predictions of the extended WM model deviate slightly from the experimental results at small times, though

TABLE I
Fitting Parameter Values of Eq. (5) for Transient Viscosity of Startup of Shearing Motion

$\dot{\gamma}$ (s^{-1})	λ_0	K
10	0.0734	0.364
1	1.014	0.285
0.1	6.274	0.041
0.01	13.544	0.00033

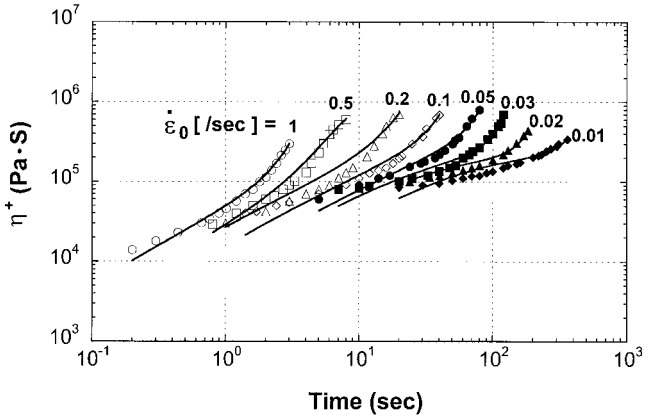

Figure 4 Comparison of the transient viscosity after startup of elongational motion in an LDPE I melt with the predictions of the modified White–Metzner model. Elongation rate $\dot{\epsilon}$ = (open circle) 1 s^{-1}, (open square) 0.5 s^{-1}, (open triangle) 0.2 s^{-1}, (open diamond) 0.1 s^{-1}, (filled circle) 0.05 s^{-1}, (filled square) 0.03 s^{-1}, (filled triangle) 0.02 s^{-1}, (filled diamond) 0.01 s^{-1}. Data of Meissner.[15–17] The solid lines are the predictions of the present model using multiple relaxation time modes. The same viscosity function as in Figure 2 was used.

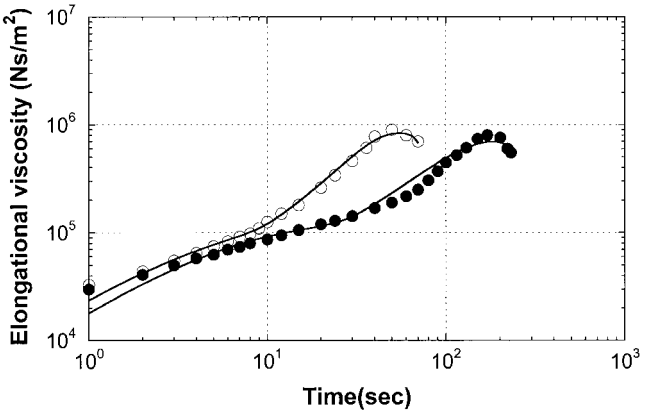

Figure 5 Elongational viscosity as a function of time, t. The solid lines are the predictions of the present model using multiple relaxation time modes. Elongation rate $\dot{\epsilon}$ = (open circle) 0.1 s^{-1} and (filled circle) 0.03 s^{-1}. Data are from Raible et al.[20]

the deviation is not serious. This is ascribable to a regression error or to the inherent nature of the material (LDPE I). Similar behavior was also observed in the theoretical results of Souvaliotis and Beris.[12] In the fitting of the startup of the shearing motion, the optimized time–parameter value (λ_0) decreases rapidly with the elongation rate, whereas K shows the opposite trend.

Interestingly enough, the present model can show the overshoot in the transient elongational viscosity, which has been experimentally observed for the same LDPE I melt[20] and which has been theoretically analyzed using a single-integral constitutive equation with a strain-dependent memory function.[21] The theoretical results and the experimental results agreed qualitatively. A comparison of the experimental results of Raible et al.[20] for the same LDPE I with the predictions of the present model using the same material parameter values above shows a fairly reasonable correlation (Fig. 5). It fits the overshooting in transient elongational viscosity pretty well, but underpredicts the transient elongational viscosities at short times. As mentioned earlier, this might be ascribed to regression errors coming from the difference of the magnitudes of the data, but a more probable reason is that it is due to the inherent properties of the polydisperse material. In order to fit the step function shear-strain experimental data for melts of the same polymer, Laun[13,14] had to use two functions for the damping function in shear. This is reasonable since the material (LDPE I) is quite polydisperse (the polydispersity index is about 22).[12] Hence, a multiple relaxation spectrum can fit the data more naturally, although it is impractical for numerical calculations.

Like the case of the viscosity function for the startup of steady-state shear flow, the good agreement with the experimental data is ascribed to the dependence of the relaxation time on the invariant of the stress tensor rather than on that of the rate of deformation tensor. Thus, the model can describe the transient behaviors of polymer melts quantitatively as well as qualitatively. This is possible because the present model satisfies the evolution condition, that is, the positive definiteness of the configuration tensor (hence that of the stress tensor invariant).[10,12]

TABLE II
Fitting Parameter Values of Eq. (5) for Transient Viscosity of Startup of Elongational Motion

$\dot{\varepsilon}$ (s^{-1})	λ_0	K
1	0.601	−0.0027
0.5	1.604	−0.0010
0.2	2.994	−0.0035
0.1	4.731	−0.012
0.05	9.036	−0.014
0.02	14.326	−0.02
0.01	27.675	−0.023

CONCLUSIONS

Proposed simple equation for the steady-state viscosities of shearing and elongational deformations is combined with the White–Metzner model following the approach of Souvaliotis and Beris,[12] who applied the generalized bracket formulation in which the relaxation time is defined as a function of the first invariant of the configuration tensor (hence that of the stress tensor). This approach, which agrees with the intent of White and Metzner in the initial derivation of the model, provides a good correlation between the

experimental data and the theoretical predictions. The model predictions are examined in fitting transient flows, both shearing and extensional. The model describes the transient behaviors of polymer melts very well, quantitatively as well as qualitatively. Also, the model predicts the overshoot in the transient shear viscosity very well. Instead of a single relaxation time model, multiple relaxation spectrum, which is physically reasonable though impractical in numerical simulation, could give us very good correlation with experimental data. For the transient elongational stress growth, using the same relaxation spectrum fitting for transient shear data did not give a good fitting for transient elongational viscosity data. Addition of more terms to the relaxation time function improves the agreement remarkably, especially at short times. The model shows a fairly good correlation around the overshoot at long times, but also shows a slight deviation at short times. This is ascribable to the regression error and/or more probably to the polydisperse material's inherent properties. Because of the inherent functional property, present model prediction approaches that of linear viscoelasticity at low deformation rates. The values of the parameters obtained are physically reasonable, and their trends are in agreement with those of the parameters obtained by Souvaliotis and Beris.[12]

This study corroborates the proposition of Souvaliotis and Beris[12] that a model whose constants are functions of the invariants of the internal tensorial structural parameter, a configuration tensor (hence those of the stress tensor), leads to qualitatively and quantitatively reasonable predictions, including the overshoots in the transient shear viscosity and the transient elongational viscosity.

The author expresses his gratitude to Dr. Eunwon Han for helpful discussion. Special thanks go to Youngwook Seo and Youngin Seo for their help in article preparation.

References

1. Larson, R. G. Constitutive Equations for Polymer Melts and Solutions; Butterworths: Boston, 1988.
2. Bird, R. G.; Armstrong, R. C.; Hassager, O. Dynamics of Polymeric Liquids, 2nd ed., Vol. 1; Wiley: New York, 1987.
3. Seo, Y. J Non-Newtonian Fluid Mech 1994, 51, 179.
4. Seo, Y. J Appl Polym Sci 1994, 52, 629.
5. Wagner, M. H. Rheol Acta 1977, 16, 43.
6. White, J. L.; Metzner, A. B. J Appl Polym Sci 1963, 7, 1867.
7. Barnes, H. A.; Roberts, G. P. J Non-Newtonian Fluid Mech 1992, 44, 113.
8. Ide, Y.; White, J. L. J Non-Newtonian Fluid Mech 1977, 2, 281.
9. Beris, A. N.; Edwards, B. J. J Rheol 1990, 34, 55.
10. Dupret, F.; Marshal, J. M. J Non-Newtonian Fluid Mech 1986, 20, 143.
11. Joseph, D. D.; Saut, J. C. J Non-Newtonian Fluid Mech 1986, 20, 20.
12. Souvaliotis, A.; Beris, A. N. J Rheol 1992, 36, 241.
13. Laun, H. M. Rheol Acta 1978, 17, 1.
14. Laun, H. M. J Rheol 1986, 30, 459.
15. Meissner, J. J Appl Polym Sci 1972, 16, 2877.
16. Meissner, J. Rheol Acta 1971, 10, 230.
17. Meissner, J. Rheol Acta 1975, 14, 201.
18. Takahashi, M.; Masuda, T.; Onogi, S. J Rheol 1978, 22, 285.
19. Raible, T.; Demarmels, A.; Meissner, J. Polym Bull 1979, 1, 397.
20. Wagner, M. H.; Raible, T.; Meissner, J. Rheol Acta 1979, 18, 427.
21. Khan, S. A.; Larson, R. G. J Rheol 1989, 31, 207.