

# Semiempirical Models for Steady-Shear Viscosity and Prediction of First Normal Stress Function

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## SYNOPSIS

In order to describe viscosity function behavior dependent on shear rate in steady-shear flow and to predict the first normal stress function without using discrete relaxation time spectrum, we combined the microscopic entanglement concept based on Graessley's entanglement network theory with the macroscopic constitutive model. The viscosity function derived from the entanglement model has three adjustable parameters and it was assumed to have the form of the inverse cotangent function of the shear rate. Then the first normal stress function is obtained using the Wagner's relationship. The model prediction for the first normal stress coefficient is compared with experimental data of polymer melts. Even though viscosity function and the first normal stress function vary over a wide range of shear rate, they were in good agreement for polymer melts at high shear rate. First normal stress function do not show any numerical artifacts. However, discrepancy in the first normal stress function occurs at low shear rate. This is due to the irreversibility of the entangled molecule's motion that was not taken into consideration in the entanglement model. Irreversible nonaffine motion is introduced by adding a term similar to the White-Metzner model's irreversible factor. Addition of irreversibility in the calculation of the first normal stress function considerably improves the agreement. Other comparisons are also presented and related discussions are given. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

To characterize the steady-shear flow of "simple" incompressible fluids, it is well known that three independent stress functions, shear stress and the first and second normal stress difference, are sufficient.<sup>1</sup> From these functions, three important material functions for the flow are obtained, viscosity function defined as the ratio of shear stress to shear rate and the first and second normal stress function defined as the ratio of the first and second normal stress difference to the square of the shear rate. For some fluids the viscosity and the normal stress functions can vary with the shear rate by a factor of a few orders. The viscosity and normal stress functions of molten thermoplastics or polymer solutions decrease with the shear rate. At low shear rates, viscosity approaches the "zero shear viscosity" and then it decreases in the so-called "power-law"

region.<sup>2</sup> The first and second normal stress functions are known to similarly behave as the viscosity function.

To represent the appearance of the viscosity versus shear rate, many models were suggested such as the power-law model,<sup>3</sup> Cross model,<sup>4</sup> Bueche-Harding model,<sup>5</sup> Ellis model,<sup>6</sup> Eyring model,<sup>7</sup> and Carreau-Yasuda model<sup>8,9</sup> to name a few. The Eyring model has a theoretical basis and others were produced by empiricism. The strong dependence of polymer viscosity on shear rate is attributed to the strong effect of shearing on entanglements. This was studied and explored by many researchers experimentally and theoretically.<sup>10</sup>

The first normal stress function is related to the elasticity of fluid.<sup>2</sup> From many constitutive relationships, it should be noted that the first normal stress function is also a decreasing function of the shear rate as is the second normal stress function, even though the prediction does not generally show excellent agreement with experimental results.<sup>10</sup>

Some time ago, Graessley<sup>11</sup> derived an equation

for the steady-state viscosity in shear flow based on the entangled molecular theory. It was a kind of implicit expression and did not get much attention. Even though there are many simple expressions for the viscosity of shear flow, we used Graessley's idea to represent the shear viscosity dependence on the shear rate. There are three reasons for doing this. The first is to adopt an expression from the molecular entanglement concept. This gives a more plausible expression rather than a random empirical equation. The second reason is to investigate the effect of molecules's nonaffine motion (chain retraction) not considered in Graessley's model. The final reason is to apply Wagner's relationship to get the first normal stress function values from the shear viscosity data. Stastna and DeKee<sup>12</sup> have compared several relationships proposed to calculate the first normal stress coefficient,  $\Psi_1$  from the viscosity,  $\eta$ . These are based on empirical constitutive equations, and some success in their application has been claimed. However, they conclude that such procedures do not have universal applicability to polymeric fluids. We will correlate the viscosity and the first normal stress coefficient using the same parameter values and Wagner's relationship.

This is an *ab initio* study to search for a useful expression for the steady shear viscosity and for the relation to appropriately predict the first normal stress function.

## THEORETICAL BACKGROUNDS

An approximate molecular theory of steady flow in amorphous polymers was developed by Graessley<sup>11</sup> after considering the properties of a deforming entanglement network. The viscosity of a polydisperse, highly entangled system at finite rates of deformation can be expressed formally in terms of integrals involving two functions.<sup>11</sup> One function is the ratio  $g(\dot{\gamma}, m)$ , the average number of entanglement junctions for a chain of length  $m$  in a steady flow field of shear rate  $\dot{\gamma}$ , divided by the number in the limit of  $\dot{\gamma} = 0$ . The other function is also a ratio  $h(\dot{\gamma}, m)$ , the rate of energy dissipation by a chain of length  $m$  in a system with shear rate  $\dot{\gamma}$  and some prescribed communal friction coefficient  $\zeta$  divided by  $\dot{\gamma}^2$ , divided by the value of that same quantity at the same value of  $\zeta$  but in the limit of  $\dot{\gamma} = 0$ . Graessley expressed  $g(\dot{\gamma}, m)$  and  $h(\dot{\gamma}, m)$  by considering the probability of entanglement formation.<sup>11</sup> Supposing the probability is inversely proportional to the square of flow direction distance, which seems more

reasonable to consider the molecular weight distribution form,<sup>13</sup> we get the following equations;

$$g(\dot{\gamma}, m) = \frac{2}{\pi} \cot^{-1}\theta \quad (1)$$

$$h(\dot{\gamma}, m) = \frac{2}{\pi} \left\{ \cot^{-1}\theta - \frac{\theta}{1 + \theta^2} \right\} \quad (2)$$

where  $\theta = (1/2)\dot{\gamma}\tau(\dot{\gamma}, m)$ . These are slightly different from the original Graessley's equations. The time  $\tau$  was taken to be the order of the Rouse relaxation-time parameter, evaluated at the existing rate of deformation.<sup>11</sup> For small  $\theta$ ,  $h(\dot{\gamma}, m) = 1$  and for large  $\theta$ , it is proportional to  $\cot^{-1}\theta$ . After the expansion of eqs. (1) and (2) in series form, we may write the general viscosity function in monodisperse system as

$$\eta/\eta_0 = f(\cot^{-1}\theta) \quad (3)$$

implicating all assumptions to be in the functional form. At large value of  $\theta$ , however, higher order terms of  $\cot^{-1}\theta$  in eq. (9) diminish more rapidly than the first-order term. Hence discarding higher order terms than the first order presents a simple equation.

$$\eta = c_1 + c_2 \cot^{-1}(\lambda\dot{\gamma}) \quad (4)$$

where  $c_1$  and  $c_2$  are constants and  $\lambda$  is another function of  $\dot{\gamma}$  and  $m$ . Intuitively, we feel that a formula like eq. (4) is a corresponding form to the Rouse model because the Rouse model represents a Brownian motion of coupled oscillators of which motions are expressed in trigonometric function form.<sup>14</sup> As shown later, however, this function form is also related to other constitutive equations derived from continuum mechanics theory. By changing the relaxation time parameter from the Rouse relaxation time to characteristic time of the system  $\lambda$ , we can relax the requirement that the value of  $\tau_0$ , the relaxation time at zero of deformation, is correlated with the corresponding Rouse parameters in a manner independent of molecular weight distribution. If  $\lambda$  depends on  $(\dot{\gamma}, m)$  that means implicit dependence on viscosity, eq. (4) is a complicated equation that needs numerical calculation. On the other hand, if we take  $\lambda$  as a system's characteristic relaxation time, then eq. (4) can explicitly describe the behavior of viscosity function.

Until now, we derived a viscosity functional form based on the idea from the entanglement theory. Then using the shear stress and normal stress dif-

ference relationship as Graessley did,<sup>11</sup> we can calculate the first normal stress function from the implicit viscosity functional. However, we want to get an explicit form of the first normal stress function for a more practical purpose. So we abandon Graessley's method and use the Wagner's relationship<sup>15</sup> between the viscosity function and the first normal stress function. According to Wagner, a relationship between the viscosity function,  $\eta$ , and the first normal stress function,  $\Psi_1$ , in steady-shear flow exists

$$\Psi_1(\dot{\gamma}) = -\frac{1}{n} \frac{\partial \eta(\dot{\gamma})}{\partial \dot{\gamma}}. \quad (5)$$

Putting eq. (4) into eq. (5) presents the first normal stress function as following:

$$\Psi_1(\theta) = \frac{1}{n} \frac{c_1 \lambda}{1 + (\lambda \dot{\gamma})^2}. \quad (6)$$

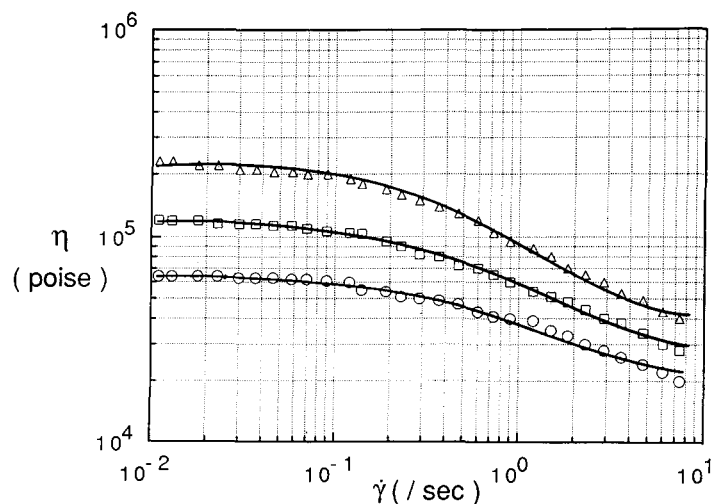
This function is similar to the first normal stress coefficient of the so-called "corotational Maxwell model."<sup>14</sup> Therefore, if we are able to deduce the semiempirical viscosity function from the experimental data, then we can also obtain the first normal stress function, which enables us to use the constitutive equation from continuum mechanics such as the K-BKZ model.<sup>16,17</sup>

## CALCULATION AND COMPARISON WITH EXPERIMENT

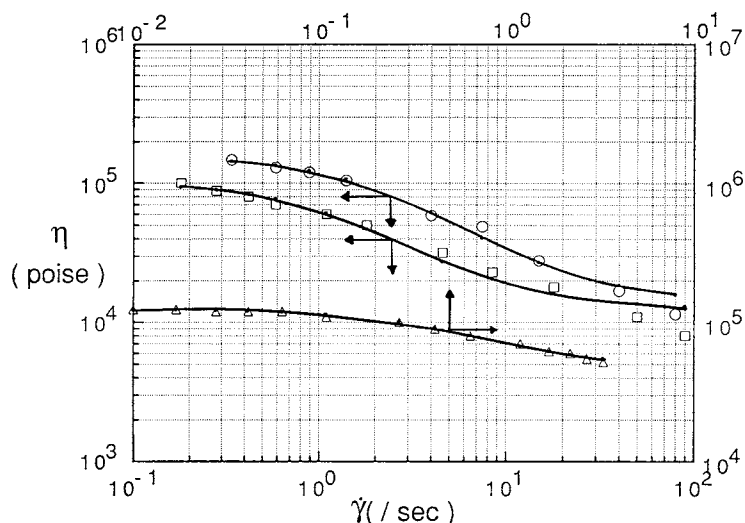
In order to see how the model works, first we fit experimental data used by Bird et al.<sup>18,19</sup> and Wag-

ner.<sup>15</sup> The shear viscosity function  $\eta$  for six polymer melts versus the shear rate are shown in Figures 1 and 2. The fitting parameter values are presented in Table I.<sup>20-22</sup> The solid lines are optimized fittings. Agreement between predicted and measured values is quite good. The intrinsic property of inverse cotangent function presents a sigmoidal curve that at high shear rate reaches a constant value similar to infinite shear rate viscosity. Provided the viscosity data could be obtained through the whole region of the shear rate region, which has been done seldomly due to measuring instrument limit, this function can qualitatively describe the viscosity function behavior from low shear rate, through the power-law region and to infinite shear rate. However, inverse cotangent function has the limit in fitting the polydisperse system, especially when the molecular weight distribution is very broad. This is due to the explicit expression of the relaxation time that takes account of the nonlinearity between the viscosity and the shear rate. For very polydisperse polymer melts, the viscosity function varies a few orders of magnitude in a wide range of shear rate.<sup>23</sup> For monodisperse polymer, shear rate variation seldom goes over two or three decades in transition region. Inverse cotangent function works well for the polymer melts whose transition region is narrow. If the transition region expands over four decades of shear rate, inverse cotangent function converges to a constant value.

Figures 3 and 4 show the normalized dimensionless first normal stress function for those polymer melts of Figures 1 and 2 versus the nondimensional shear rate  $\lambda_e \dot{\gamma}$ , where  $\lambda_e$  is the relaxation time from experimental data. The solid lines represent eq. (6),



**Figure 1** Viscosity function of low-density polyethylene melt (data of Chen and Bogue<sup>20</sup>): ( $\Delta$ ) 160°C; ( $\square$ ) 180°C; ( $\circ$ ) 200°C; (—) calculated values using eq. (4).



**Figure 2** Viscosity function of three polymer melts: (○) polystyrene, 180°C (data of Ballenger et al.<sup>21</sup>); (□) high-density polyethylene, 160°C (data of Ballenger et al.<sup>21</sup>); (△) phenoxy-A 212°C (data of Marsh<sup>22</sup>); (—) calculated values using eq. (4).

where the parameter values of nonlinearity,  $n$ , were Wagner's adjusted values to give best fit to the experimental data using Carreau's model<sup>15</sup> shown in Figures 3 and 4 as dotted lines. For low density polyethylene melt data (Fig. 3), agreement between predicted values of the first normal stress function and experimental data is quite encouraging. For other polymers in Figure 4, the agreement is not as good at low shear rate. These polymers are considered to have a broad molecular weight distribution

that makes it difficult to characterize the material with a single characteristic time. However, we are encouraged by the fact that artificial effects in the prediction of the first normal stress function that appeared in the Carreau's viscosity equation<sup>15</sup> does not occur in the current model's prediction. Because the viscosity function has the shape of the inverse cotangent function, its derivative never produces a maximum point. Inflection points of the Carreau's model in viscosity function prediction caused arti-

**Table I** Properties of Test Fluids and Parameters Used for Fitting

Polymer Melts	$T$ (°C)	Carreau's Viscosity Equation Parameters <sup>a</sup>			Damping Constant, $n^b$	Parameters Used in eq. (4)		
		$\eta_0$ (Poise)	$\lambda_e$ (s)	$N$		$c_1$	$c_2$	$\lambda$
Low-density polyethylene <sup>20</sup>	160	2.32E5	7.18	0.24	0.13	4.093E4	1.156E5	2.303
Low-density polyethylene <sup>20</sup>	180	1.21E5	5.23	0.217	0.13	3.04E4	5.7E4	2.196
Low-density polyethylene <sup>20</sup>	200	6.43E4	2.86	0.207	0.13	2.109E4	2.73E4	1.505
High-density polyethylene <sup>21</sup>	160	8.92E4	1.58	0.252	0.2	1.218E4	5.678E4	0.79
Polystyrene <sup>21</sup>	180	1.48E5	1.04	0.301	0.2	1.31E4	9.1E4	0.432
Phenoxy A <sup>22</sup>	212	1.24E5	7.44	0.136	0.18	4.688E4	4.91E4	1.92

<sup>a</sup> Carreau's viscosity equation is

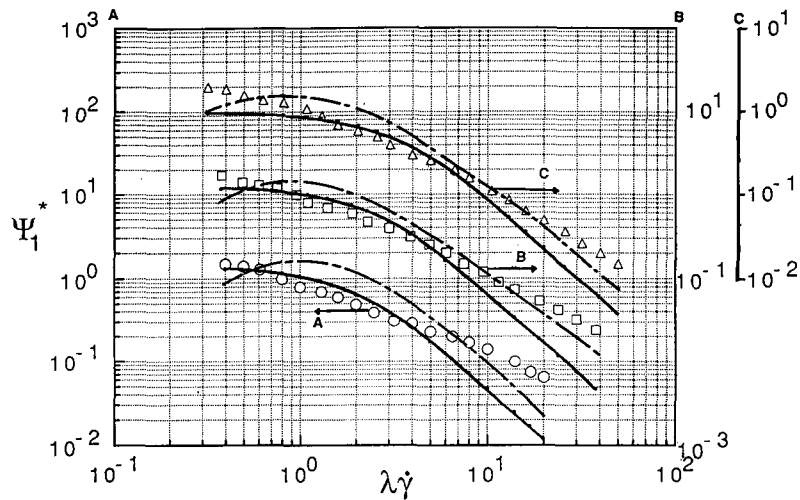
$$\frac{\eta}{\eta_0} = [1 + (\lambda_e \dot{\gamma})^2]^{-N}$$

and the first normal stress function is derived as

$$\frac{\Psi_1}{\lambda_e \eta_0} = \frac{2N}{n} \lambda_e \dot{\gamma} [1 + (\lambda_e \dot{\gamma})^2]^{-(N+1)}$$

where  $\lambda_e$  is the relaxation time and  $\eta_0$  is the zero shear rate viscosity. Infinite shear rate viscosity was assumed to be zero (see Wagner<sup>15</sup>).

<sup>b</sup> Damping constant values,  $n$ , are those used by Wagner.<sup>15</sup>



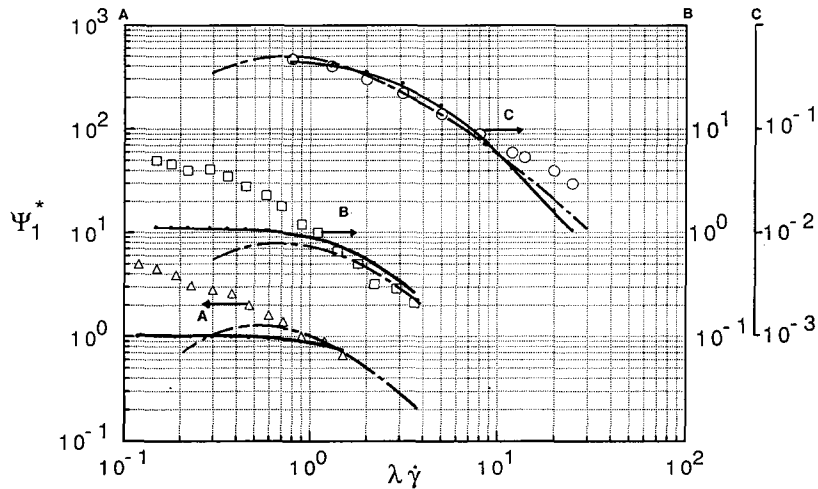
**Figure 3** Normalized first normal stress function ( $\Psi_1^* = \pi\Psi_1/4\lambda_e(\eta_0 - \eta_\infty)$ , where  $\eta_0$  is zero shear rate viscosity,  $\eta_\infty$  is infinite shear rate viscosity, and  $\lambda_e$  is the relaxation time used for Carreau's model (see footnote of Table I) for low density polyethylene melt (data of Chen and Bogue<sup>20</sup>): ( $\Delta$ ) 160°C; ( $\square$ ) 180°C; ( $\circ$ ) 200°C; (---) predicted values using Carreau's viscosity function (Wagner<sup>15</sup>); (—) predicted values using eq. (6).

ficial maxima in the first normal stress function calculation.<sup>15</sup>

## ADDITION OF CHAIN RETRACTION AND DISCUSSION

Some factors are believed to have affected the current model's first normal stress coefficient prediction. The first is these polymers have broad molec-

ular weight distribution, which hampers the current model from fitting the experimental data with only one characteristic time. In this sense, Wagner's finite series approach is worthy of consideration. Using five relaxation times, Wagner<sup>15</sup> could get markedly improved agreement. However, even though using a discrete spectrum is a reasonable approach to fit the experimental data, it requires too many parameters, which is not practical to be used in the simulation. The second factor we should take into con-



**Figure 4** Normalized first normal stress function for three polymer melts,  $\Psi_1^*$  is the same as in Figure 3: ( $\circ$ ) polystyrene, 180°C (data of Ballenger et al.<sup>21</sup>); ( $\square$ ) high-density polyethylene, 160°C (data of Ballenger et al.<sup>21</sup>); ( $\Delta$ ) phenoxy-A, 212°C (data of Marsh<sup>22</sup>); (---) predicted values using Carreau's viscosity function (Wagner<sup>15</sup>); (—) predicted values using eq. (6).

sideration is that we used the oversimplified form for the approximation of viscosity function in that we kept only the first-order term in eq. (4). However, higher order terms would affect the prediction of the first normal stress coefficient at high shear rates not at low shear rates. The other factor we did not take into consideration is the nonaffine motion. The strands of polymers slip with respect to the deformation of the macroscopic continuum. This changes the formula for the stress tensor when the motion becomes nonaffine.<sup>24</sup> The K-BKZ model that Wagner used is thermodynamically reversible, in principle, if the deformation and its reversal occur rapidly enough. According to the constitutive equation, all works exerted to deform the material can be recovered in the reversal of the deformation. However, the nonaffine motion should not be regarded as reversible. This is evident from Wagner and Meissner's work<sup>25</sup> that excellent agreement in recoverable elongational strain after prior steady elongation for low-density polyethylene is obtained when irreversibility is included in the integral equation. The nonaffine motion also produces shear thinning and strain softening that is a relaxation process that occurs faster than the deformation.

An irreversible constitutive equation was considered by Wagner (Wagner's second model)<sup>26</sup> and White and Metzner<sup>27</sup> in a different way. While Wagner incorporated the irreversibility in the damping functional having the minimum value to remove the anomaly in the reversing step strain experiment, White and Metzner noted that high strain rates should reduce the relaxation time by which the shear viscosity decreases with increased  $\dot{\gamma}$  if  $\lambda$  is a decreasing function of the second invariant in the steady shear flows. The obvious advantage of the White and Metzner model is that it has the flexibility to predict the shear viscosity and the first normal stress difference of any polymeric fluid using only one relaxation time that can obviate the use of relaxation time spectrum. Ide and White<sup>28</sup> proposed the following equation for the relaxation time in steady flows.

$$\lambda_{\text{WM}}(\Pi_{\mathbf{D}}) = \frac{\lambda_0}{1 + a\lambda_0(2\mathbf{D}:\mathbf{D})^{1/2}} \quad (7)$$

where  $\lambda_0$  is the relaxation time at zero shear rate,  $a$  is an empirical parameter, and  $\mathbf{D}$  is the deformation rate tensor. Using this form for  $\lambda_{\text{WM}}(\Pi_{\mathbf{D}})$ , the steady-state viscosity and the first normal stress coefficient of the White-Metzner model are obtained as follows:

$$\eta = \frac{G\lambda_0}{1 + a\lambda_0\dot{\gamma}} \quad (8)$$

$$\Psi_1 = \frac{2G\lambda_0^2}{(1 + a\lambda_0\dot{\gamma})^2}. \quad (9)$$

Except for the dependence of relaxation time on the second invariant of the deformation tensor, the White-Metzner model follows the upper-convected Maxwell equation, which is the same type as the K-BKZ model we used.<sup>10</sup> Taking into consideration the irreversibility of the nonaffine motion, we add one term like eq. (8) to the viscous function of which the first derivative about shear rate is similar to that of the first normal stress function of the White-Metzner model, eq. (9). The following viscosity function, a five constant model, is tried

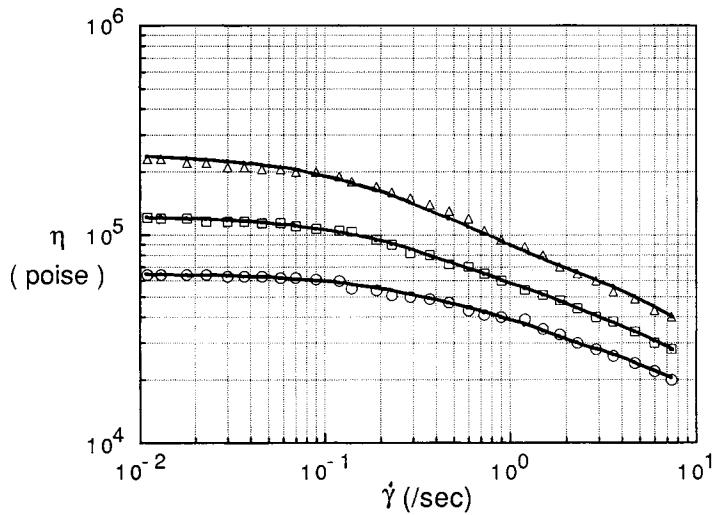
$$\eta = c_1 + c_2 \cot^{-1}(\lambda_1\dot{\gamma}) + \frac{c_3}{1 + \lambda_2\dot{\gamma}} \quad (10)$$

where  $\lambda_1$  and  $\lambda_2$  are relaxation times for affine and nonaffine motion, respectively. Figures 5 and 6 show the viscosity function calculation, which again show good agreement with experimental data. Then using eq. (5), we calculate the first normal stress function as the following equation:

$$\Psi_1 = \frac{1}{n} \frac{c_2\lambda_1}{1 + (\lambda_1\dot{\gamma})^2} + \frac{1}{n} \frac{c_3\lambda_2}{(1 + \lambda_2\dot{\gamma})^2}. \quad (11)$$

Figures 7 and 8 show the first normal stress function compared with the experimental data. The parameter values are presented in Table II. The agreement is remarkably improved and quite excellent. Addition of one more term for the irreversible nonaffine motion brings this improvement especially at low shear rate. This fact coincides with the physical explanation of the White and Metzner model that the relaxation time is reduced at high strain rate and due to the reduction of relaxation time, the polymer chain rapidly relaxes at high shear rates.<sup>26</sup> It also reduces the retraction of the chain in nonaffine motion. On the other hand, at low shear rates, relaxation time is long, which would be enough for the polymer chains to retract from the macroscopic deformation (affine motion of the Doi and Edwards model<sup>24</sup>). Inclusion of nonaffine motion, therefore, naturally compensates for the difference at low shear rate.

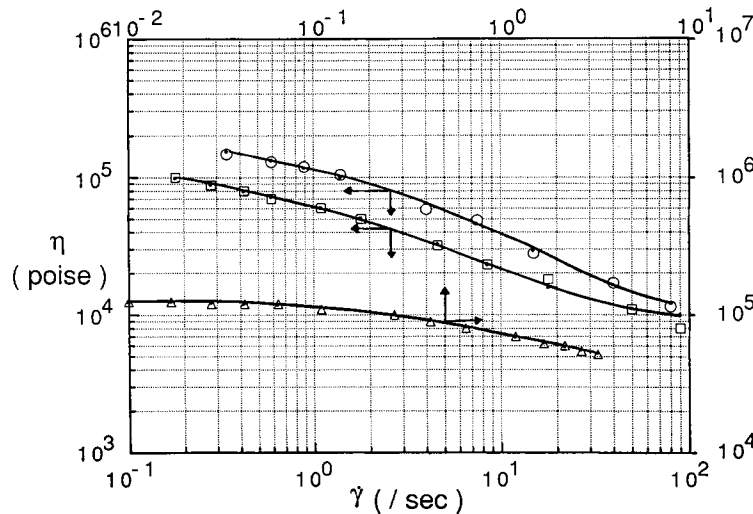
It is well known that the description of the relaxation spectrum by differential constitutive equations is of comparable significance to the description



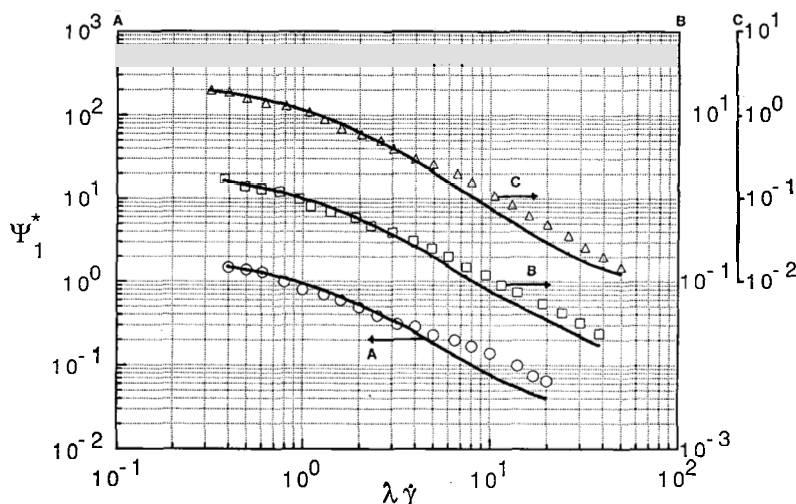
**Figure 5** Viscosity function of low-density polyethylene melt (data of Chen and Bogue<sup>20</sup>): (Δ) 160°C; (□) 180°C; (○) 200°C; (—) calculated values using eq. (10).

of the nonlinear behavior.<sup>23</sup> Although the fitting based on the superposition of the discrete mode can be successful in homogeneous flows, as the comparison with the experimental data showed, it is certainly impractical in numerical simulations of more complicated flows and excludes the possibility of direct coupling between the various modes. For the comparison with the multiple mode model, we used the experimental data of Laun<sup>29</sup> for low-density polyethylene which has a wide molecular weight distribution. This data was also used by Souvaliotis and Beris.<sup>23</sup> They proposed a phenomenological vis-

coelastic model of differential type along the lines of the White-Metzner modification where the model constants are functions of the invariants of an internal tensorial structured parameter. Power-law type relaxation time was used in their model. The comparison of Laun's experimental data with the current model are shown in Figures 9 and 10 for steady shear viscosity and the first normal stress function. In spite of the fact that the melt is highly polydispersed, the agreement is quite reasonable. Also shown are predictions of the modified White-Metzner model (MMW) and Phan-Thien and



**Figure 6** Viscosity function of three polymer melts: (○) polystyrene, 180°C (data of Ballenger et al.<sup>21</sup>); (□) high-density polyethylene, 160°C (data of Ballenger et al.<sup>21</sup>); (Δ) phenoxy-A, 212°C (data of Marsh<sup>22</sup>); (—) calculated values using eq. (10).

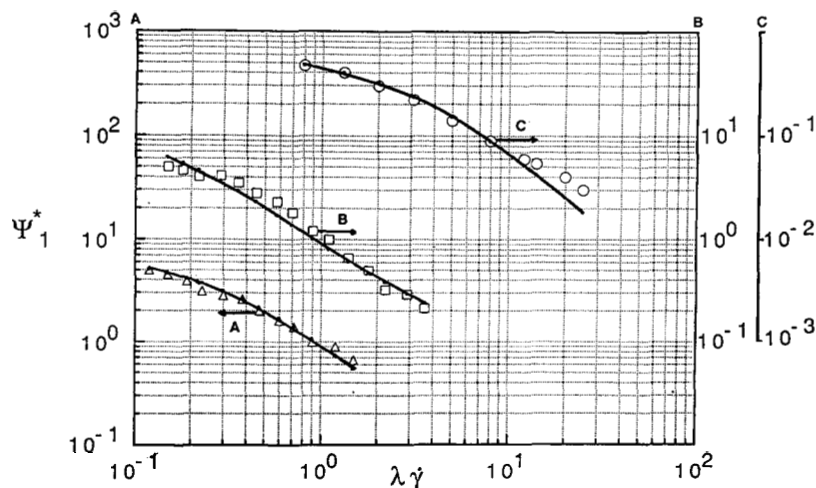


**Figure 7** Normalized first normal stress function for low-density polyethylene melt (data of Chen and Bogue<sup>20</sup>),  $\Psi_1^*$  is the same as in Figure 3: ( $\Delta$ ) 160°C; ( $\square$ ) 180°C; ( $\circ$ ) 200°C; (—) predicted values using eq. (11).

Tanner model (PTT)<sup>30</sup> by Souvaliotis and Beris. Our model shows a better performance in the experimental data fitting and demonstrates a greater flexibility. The first normal stress function shown in Figure 9 is also in good agreement. In our model, two relaxation times are optimized but its performance is better than the MMW and PTT models in which eight multiple modes were used to get the best fit. The exponents used by Souvaliotis and Beris for the viscosity data and first normal stress differ-

ence are quite different from each other, both for MMW and PTT models. We used the same parameters for the fitting of both viscosity and the first normal stress functions, which is more consistent and reasonable.

We achieved a better fitting by adding more terms for the viscosity and normal stress functions as Souvaliotis and Beris did. For example, addition of one more term having a different relaxation time in the viscosity function can overcome the intrinsic



**Figure 8** Normalized first normal stress function for three polymer melts,  $\Psi_1^*$  is the same as in Figure 3: ( $\circ$ ) polystyrene, 180°C (data of Ballenger et al.<sup>21</sup>); ( $\square$ ) high-density polyethylene, 160°C (data of Ballenger et al.<sup>21</sup>); ( $\Delta$ ) phenoxy-A 212°C (data of Marsh<sup>22</sup>); (—) predicted values using eq. (11).



**Table II** Parameter Values<sup>a</sup> Used in eq. (10) for Curve Fitting

Polymer Melts	$n^b$	$c_1$	$c_2$	$c_3$	$\lambda_1$	$\lambda_2$
Low-density polyethylene (160°C)	0.13	-2.32E4	4.885E4	1.906E5	0.058	3.892
Low-density polyethylene (180°C)	0.13	0.804E4	1.866E4	8.697E4	0.121	2.773
Low-density polyethylene (200°C)	0.13	-3.94E4	3.947E4	4.262E4	0.019	1.574
High-density polyethylene	0.2	0.84E4	3.03E4	8.846E4	0.268	5.577
Polystyrene	0.2	0.78E4	4.E4	1.39E5	0.151	1.965
Phenoxy A	0.18	-1.908E4	3.84E4	8.385E5	0.015	1.625
LDPE-I <sup>c</sup>	0.18	0.175E4	1.687E4	1.9437E4	1.611	57.00

<sup>a</sup> These are optimized values. Depending on the method of curve fitting, these values can be slightly varied.

<sup>b</sup> All  $n$  values are from Wagner<sup>15</sup> except LDPE-I which is from Laun.<sup>29</sup>

<sup>c</sup> LDPE-I is a very polydisperse and long chain branched low-density polyethylene used by Laun.<sup>29</sup>

property of the cotangent function that always shows a sigmoidal behavior when the shear rate span in the transition region is large. As a test, we tried the following equation,

$$\eta = c_1 + c_2 \cot^{-1}(\lambda_1 \dot{\gamma}) + c_3 \cot^{-1}(\lambda_2 \dot{\gamma}) + \frac{c_4}{1 + \lambda_3 \dot{\gamma}} \quad (12)$$

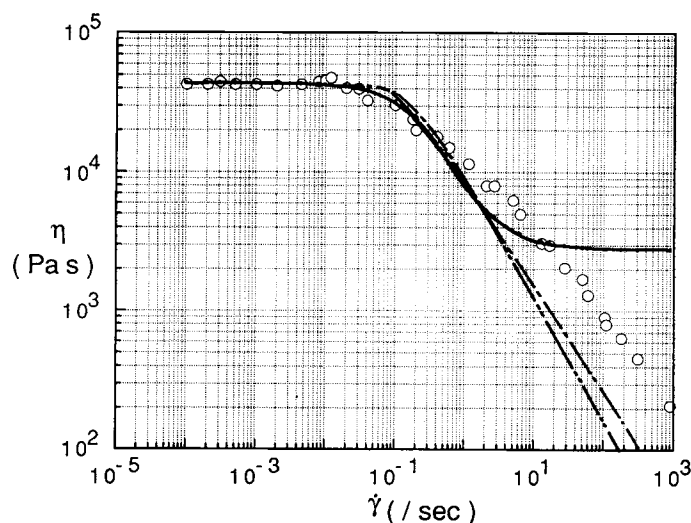
and then the first normal stress function from this function has the following form,

$$\Psi_1 = \frac{1}{n} \frac{c_2}{1 + (\lambda_1 \dot{\gamma})^2} + \frac{1}{n} \frac{c_3}{1 + (\lambda_2 \dot{\gamma})^2} + \frac{1}{n} \frac{c_4 \lambda_3}{(1 + \lambda_3 \dot{\gamma})^2} \quad (13)$$

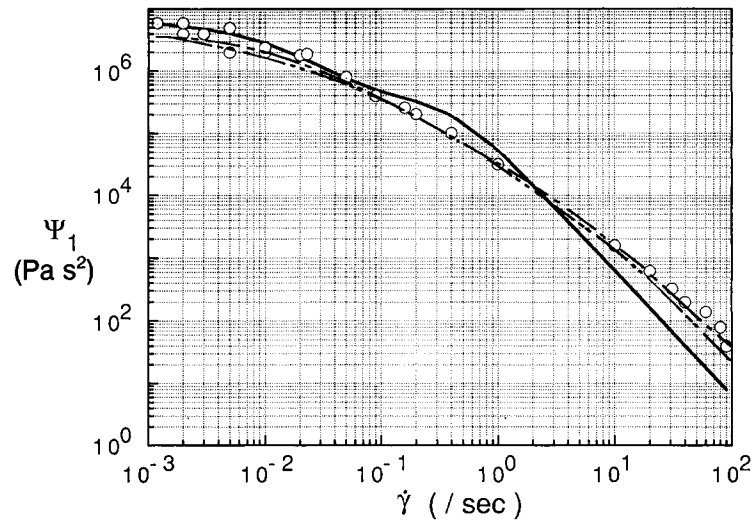
The result is shown in Figures 11 and 12. The agreement with the experimental data is excellent. The first normal stress function agrees very well with experimental data over the six decades of variation! Even more importantly, we used the same parameter values for both functions which was not possible for the MWM and PTT model<sup>23</sup> to fit the experimental data.

## CONCLUSION

Graessley's model for steady shear viscosity function was modified to express the viscosity function explicitly and accurate prediction, quantitatively as well as qualitatively, of the first normal stress function was sought using Wagner's relationship. Inverse cotangent function having three parameters can fit



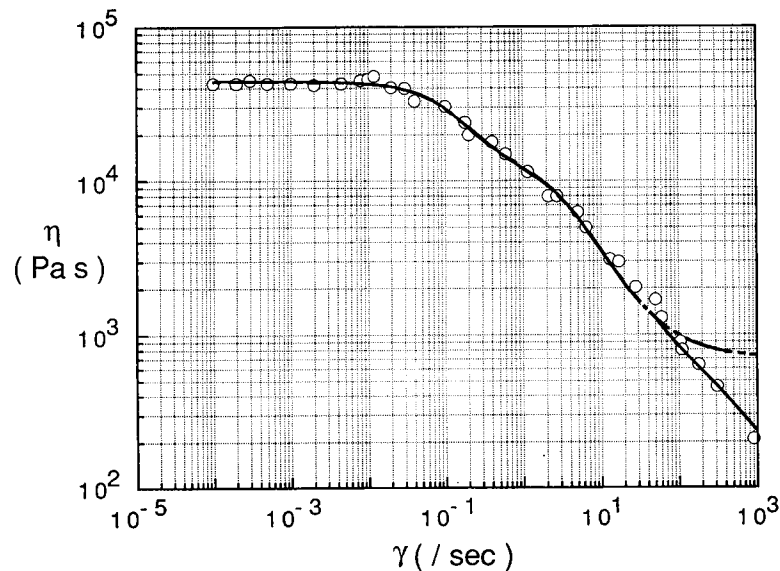
**Figure 9** Viscosity function of the low-density polyethylene I melt, (○) data of Laun<sup>29</sup> with: (---) predictions of the power-law modified White-Metzner model<sup>23</sup> ( $k = -0.54$ ); (- · -) predictions of the PTT model<sup>23</sup> ( $\epsilon = 0.01$ ); and (—) calculations of the current model, eq. (10).



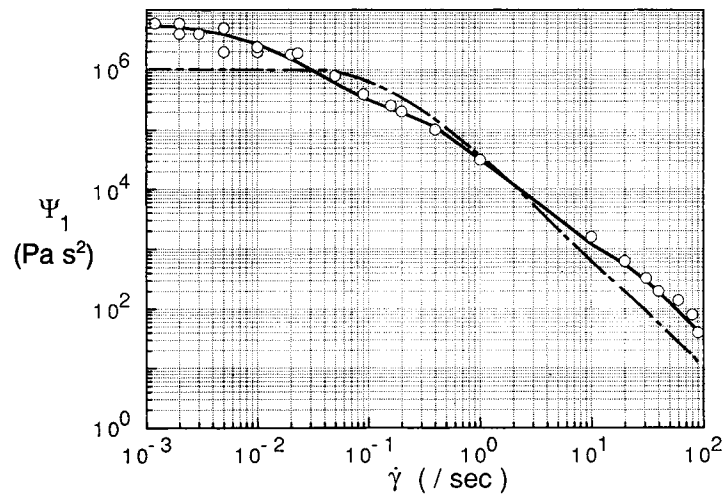
**Figure 10** The first normal stress function  $\Psi_1$  of the low-density polyethylene I melt ( $\circ$ ), data of Laun<sup>29</sup>; (---) predictions of the power-law extended White-Metzner model<sup>23</sup> ( $k = -1.6$ ); (- - -) predictions of the PTT model<sup>23</sup> ( $\varepsilon = 0.24$ ); (—) predictions of the current model, eq. (11).

the viscosity function very well. But comparison of the first normal stress function prediction with experimental data was not in good agreement at low shear rates where relaxation time is long, even though it definitely did not show any numerical artifact, which occurred in Carreau's model prediction.

The chain retraction motion not accounted for in the entanglement model was thought to be a factor. Addition of irreversible nonaffine motion similar to that of the White-Metzner model supplements this pitfall and remarkably improves the agreement. This reminds us that the long relaxation time at low shear



**Figure 11** Viscosity function of the low-density polyethylene I melt, ( $\circ$ ), data of Laun<sup>29</sup> with: (---) calculations of the current model using eq. (10). The fitting parameters values are  $c_1 = 7.04\text{E}2$ ,  $c_2 = 6.83\text{E}3$ ,  $c_3 = 2.186\text{E}4$ ,  $\lambda_1 = 0.252$ ,  $\lambda_2 = 8.56$ . (—) calculations of the current model using eq. (12). The fitting parameters values are  $c_1 = 1.93\text{E}2$ ,  $c_2 = 3.41\text{E}3$ ,  $c_3 = 1.459\text{E}4$ ,  $c_4 = 1.944\text{E}4$ ,  $\lambda_1 = 0.06$ ,  $\lambda_2 = 2.323$ ,  $\lambda_3 = 57$ .



**Figure 12** First normal stress function of the LDPE I melt, (O) data of Laun<sup>23</sup>: (—) predictions by the current model using eq. (13); (---) predictions using only the first two terms in eq. (13) ( $n = 0.18$ ); other parameter values are the same as those in Figure 11.

rates would be long enough for the polymer chains to retract from the macroscopic motion. The current model looks useful for the modeling of non-Newtonian fluid behavior in shear steady flow. We used the same parameter values for both the viscosity and the first normal stress function, which was not possible by the modified White–Metzner model or the Phan–Thien and Tanner model.

The proposed model has five parameters that might be too many to be used for practical purposes. However, the inverse cotangent function shed light on a model that can fit the viscosity function with fewer parameters and accurately predict the first normal stress function. We believe improvement can be obtained using a simple model that takes into consideration the nonlinearity between the material functions and the shear rate. This might be worthy of further investigation and new results will be reported in a separate article.<sup>31</sup>

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