

## A RHEOLOGICAL MODEL FOR POLYMER MELTS WITH INTERNAL STRUCTURE IN FLOW FIELDS\*

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**Abstract** Conceptually, an imagined conformation ellipsoid is supposed to represent the shape of a polymer chain for polymer melts in flow fields and to be equivalent to the volume element in a mathematical sense in continuum mechanics. A power law dependence of shear modulus of polymer melts on  $\det C$ , referred to as envelope volume, is proposed. Based on those assumptions and the non-linear relation of shear modulus, a phenomenological viscoelastic model is derived. The model is tested in simple shear flow, simple elongational flow, oscillatory shear flow, and relaxation process after flow suddenly stopped. The results show that the model works well to predict the change of internal structure and viscoelastic performance of polymer melts in flow fields.

**Keywords** Polymer melts, Rheological model, Polymer conformation, Flow fields

### INTRODUCTION

In order to obtain optimal properties it is essential to precisely control the internal structure of polymeric materials in processing. Polymer has multiple levels of internal structure. Among them polymer chain conformation is the most important one, because extension and orientation of that decide the viscoelasticity of the melts and morphology formation of the polymer. Therefore, much effort has been made to understand the relations between bulk flow behavior and polymer chain structure in flow fields. Over the years, a great variety of differential-type viscoelastic fluid models have been proposed in the literature<sup>[1-3]</sup>. There are two types of approaches to find the rheological relations. One is based on the theory of continuum mechanics, in which deformation gradient tensor is often used to represent the strain behavior of polymer melts. However the change of internal structure of polymer melts cannot be described directly in real dimension in this way since material continuum exists in the mathematical sense. Another method relies on polymer kinetic theory<sup>[2, 4]</sup>. Usually these kinetic models are related to the configuration distribution functions of polymer chains. There exist some difficulties in applying these models to the engineering problems in the industry due to mathematical complexity. Therefore, molecular kinetic theory of polymer has concentrated on simple models that include only the most basic characteristics of polymer molecules. Those models, such as the rigid dumbbell model, FENE (finitely extendable nonlinear elastic) model, etc., are very helpful in understanding rheological properties. The usual drawback, however, is failure to predict the slopes of viscosity and first normal stress coefficient versus shear rate in power-law region. Thus they do not permit a more quantitative comparison with

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experimental results.

In polymer processing we need a constitutive model of polymer melts which is simple and has a clear physical meaning with internal structure. Motivated by the need for a quantitative description of the behavior of internal structure and viscoelastic effects during melt processing, the author has attempted to combine the above two methods to provide a constitutive model with internal structure for polymer melts in flow fields.

The power law is often used to describe non-Newtonian viscoelastic behavior of polymer melts in the modified Maxwell models (for example, White-Metzner model). In these models, both viscosity  $\eta$  and relaxation time  $\lambda_1$  are assumed to be a function of the second invariant of the deformation rate tensor  $\dot{\gamma}$  or the second invariant of the stress matrix. They are related by elastic modulus  $G$ :  $\lambda_1 = \eta/G$ . However, the power law dependence on  $\dot{\gamma}$  can be valid in some special cases, such as small strain field, but fails in more general flow fields. To solve the non-linear problem a power-law dependence of the relaxation time on the trace of the tensorial internal parameter was proposed and a multiple mode version was used in fitting experimental data obtained for polymer melts<sup>[5]</sup>. However, the index  $k$  for non-linear property was adopted arbitrarily in their paper: for viscosity,  $k = -0.54$ ; for first normal stress coefficient  $k = -1.6$ . Thus it is impossible to apply their model to the practical problems encountered in polymer processing. In our previous works<sup>[6, 7]</sup>,  $G$  was assumed to be a constant, and the non-linear property of polymer melts was introduced by the anisotropic Brownian motion parameter and the anisotropic drag force parameter. In this paper, a power law dependence of shear modulus of polymer melts on  $\det C$ , referred to as envelope volume, is proposed. The parameter for this non-linear relation is just equal to the flow index of the power law for non-Newtonian fluids. Therefore the new model will be easy to use. According to this non-linear relation of shear modulus, the phenomenological model is tested in simple shear flow, simple elongational flow, oscillatory shear flow, and the relaxation process after the flow suddenly stopped.

RHEOLOGICAL MODEL

Conceptually, polymer chains in the melt can be imagined as an intercrossed viscoelastic matrix. The allowed possible conformation of the representative polymer chain is almost confined in an imagined sphere-like region as shown by the line in Fig. 1. Suppose for a moment that the other chains are frozen, then the dots within the sphere can be regarded as fixed obstacles. The sphere is referred to as a conformation sphere, which is deformable in flow. When shear rate (or extension rate) increases, the polymer chain will extend and orient, thus the conformation sphere is changed into a conformation ellipsoid. Finally, the ellipsoid becomes a conformation pipe when shear rate (or extension rate) is very high (see Fig. 1).

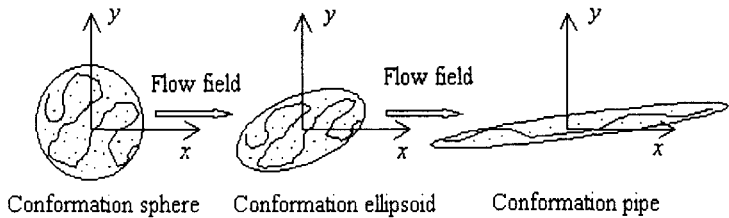


Fig. 1 Schematic illustration of conformation sphere in flow field

The author assumes that the control element in mathematical sense in continuum mechanics is equivalent to the conformation ellipsoid that is represented by the elastic dumbbell model, and denoted by a tensor. Thus the following expressions for free energy  $A$  and dissipation tensor  $A_{ijkl}$

can be obtained:

$$A = \frac{\lambda}{2} \left[ \text{tr} \left( \frac{\delta - C}{2} \right) \right]^2 + G \left[ \text{tr} \left( \frac{\delta - C}{2} \right) \right]^2 \quad (1)$$

$$A_{ijkl} = \frac{8}{n\zeta} C_{ik} \delta_{jl} \quad (2)$$

where  $\lambda$  is the elastic constant related to compression modulus,  $G$  the shear modulus,  $\delta_{ij}$  unit tensor,  $n\zeta$  molecular friction force per unit volume,  $C_{ij}$  the internal structure tensor.  $C_{ij} = \int R_i R_j \psi dR / R_0^2$ , where  $\psi$  is a configuration distribution function,  $R_i$  is a vector describing the internal structure of polymer chain<sup>[8]</sup>,  $R_0$  is a scalar of  $R_i$  at rest.  $C_{ij}$  may be referred to as a conformation tensor when  $R_i$  is the vector representing end-to-end vector or radius of gyration of polymer chain.

As a polymer chain is extended and oriented, the free energy as well as the recoverable force of the chain increases. This means that more force is needed to extend a similar degree of the chain to overcome the recovery force. Therefore shear modulus  $G$  should be increased with chain extension. A simple power law relation between  $G$  and  $\det C$  is proposed:

$$G(C) = G_0 / (\det C)^\alpha \quad (3)$$

where  $G_0$  is the modulus at rest,  $\alpha = 1 + n$ .  $n$  is flow index of the power law model, which can be measured by rheometers easily. The envelope volume  $\det C$ , i.e. determinate of  $C_{ij}$ , is proportional to the volume of the conformation ellipsoid. When  $\det C$  decreases, the volume of the conformation ellipsoid decreases and  $G$  increases, which also means that chain segments are excluded from the ellipsoid and polymer chains are disentangled at same time. Therefore the computation of  $\det C$  provides a possibility to represent the entangled degree of polymer chains in flow fields.

Following the Hamiltonian-Poisson bracket formulation<sup>[9]</sup>, the evolution equation of the internal structure tensor of the polymer chain is obtained:

$$\frac{\partial C_{ij}}{\partial t} = C_{ik} \nabla_k U_j + C_{jk} \nabla_k U_i - B(C_{ik} C_{kj} - C_{ij}) \quad (4)$$

where  $t$  is time,  $U_i$  is velocity,  $B = G/(\eta_0 \dot{\gamma}) = 1/S_R$ ,  $\dot{\gamma}$  is shear rate,  $S_R$  is recoverable shear. It is obvious from Eq. (4) that  $C_{ij}$  is decided by the velocity gradient  $\nabla_i U_j$ , the recoverable shear  $S_R$  and time  $t$ .

The stress tensor  $\sigma_{ij}$ , viscosity  $\eta$ , first normal stress coefficient  $\psi_1$ , and second normal stress coefficient  $\psi_2$  are expressed as follows:

$$\sigma_{ij} = G(C_{ik} C_{kj} - C_{ij}) \quad (5)$$

$$\eta = \sigma_{12} / \dot{\gamma}, \quad \psi_1 = (\sigma_{11} - \sigma_{22}) / \dot{\gamma}^2, \quad \psi_2 = (\sigma_{22} - \sigma_{33}) / \dot{\gamma}^2 \quad (6)$$

Equations (4)–(6) constitute a rheological model of the internal structure of polymer melts in flow fields.

## PREDICTIONS AND DISCUSSIONS

According to Eqs. (4)–(6), the following expressions and figures are obtained in different flow fields. LDPE was used as a model polymer in the computation of the above equations hereafter. The concerned parameters for computing internal structure and viscoelastic properties of LDPE are as follows: molecular weight  $M_w = 2.0 \times 10^5$ , zero-shear-rate viscosity  $\eta_0 = 46000$ , zero-shear-rate first normal stress coefficient  $\psi_{10} = 1.95 \times 10^6$ , flow index  $n = 0.4$ , temperature  $T = 423$  °K. Those data were recovered from Figure 3.3-2 of Ref.[1].

### Simple Shear Flow

$$\begin{aligned} C_{11} &= (2S_R^2 + 1)/(1 + S_R^2), & C_{22} &= 1/(1 + S_R^2), \\ C_{33} &= 1, & C_{12} &= S_R/(1 + S_R^2) \end{aligned} \quad (7)$$

$$\eta = \eta_0 / (1 + S_R^2), \quad \psi_1 = 2\lambda_1 \eta_0 / (1 + S_R^2) \tag{8}$$

When  $\dot{\gamma} \rightarrow 0$ ,  $\eta = \eta_0$  and  $\psi_1 = 2\lambda_1 \eta_0$ . The form in Eq. (8) is the same as in the DeWitt model. However,  $S_R$  in Eq. (8) is related to  $\det C$ , which is a way to describe the non-linear property of the polymer chain. A comparison between the predictions of the model and experimental data for the viscoelasticity of LDPE in shear flow is expressed in Fig. 2. The experimental data in the figure were recovered from the reference<sup>[1]</sup> by UN-SCAN-IT software. The results show that the model works well. The slope of the experimental curve in power-law region is not constant due to a high degree of polydispersity of the LDPE sample. The author takes average value of the slope, i.e.  $n = 0.4$ . This may be the cause of the deviation of the predictions from the experimental data. The influence of the value of  $n$  on the rheological curve is expressed in Fig. 3. The prediction curve fits

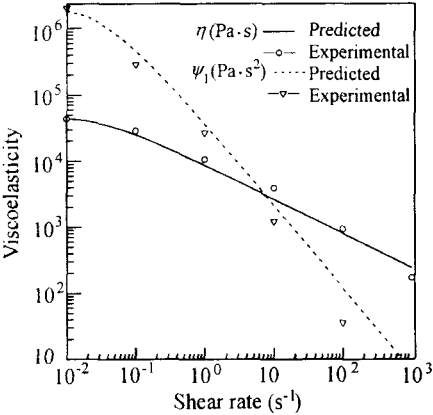


Fig. 2 A comparison between the predictions of the model and experimental data

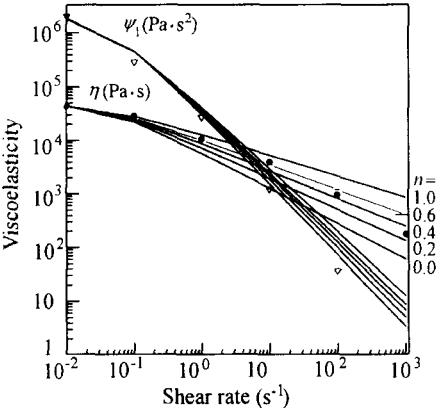


Fig. 3 The influence of flow index  $n$  on the rheological curve at different shear rates

the experimental data well approximately at  $n = 0.4$ . Figure 4 shows that both  $\eta$  and  $\psi_1$  are proportional to  $\det C$ , though the slopes of the curves are different. The decrease of viscosity  $\eta$  in power-law region stands for the disentanglement of polymer chains, therefore, the envelope volume  $\det C$  may represent the degree of the entanglement of polymer chains in the flow fields, which changes between 1–0. The change of the components of conformation tensor with shear rate is expressed in Fig. 5.  $C_{11}$  represents the degree of the chain extension, while  $C_{12}$  is related to the

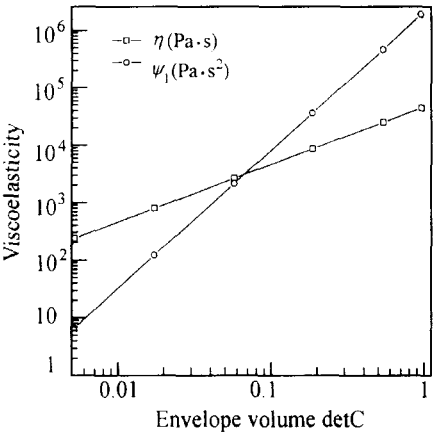


Fig. 4 A plot of viscoelasticity versus envelope volume  $\det C$

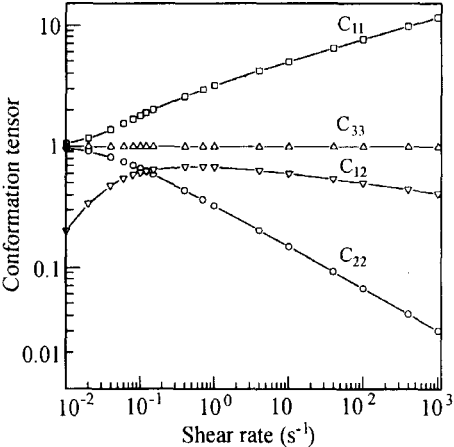


Fig. 5 A plot of conformation tensor versus shear rate

orientation of the chain. The evolution of  $C_{11}$  at different shear rates is illustrated in Fig. 6. The curves at high shear rate exhibit the overshooting phenomena. When shear rate reaches  $1000 \text{ s}^{-1}$ , an oscillation of the curve occurs, which is likely the behavior of an elastic material.

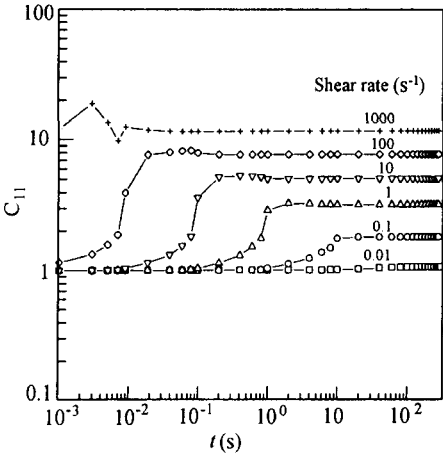


**Fig. 6** A plot of the component of the conformation tensor  $C_{11}$  versus time at different shear rates

### Simple Elongational Flow

$$C_{11} = \frac{2E_R + 1}{1 + 2E_R \exp[-(2E_R + 1)t/\lambda_1]}$$

$$C_{22} = C_{33} = \frac{1 - E_R}{1 - E_R \exp[-(1 - E_R)t/\lambda_1]} \quad (9)$$

Where  $E_R = \lambda_1 \dot{\epsilon}$ ,  $\dot{\epsilon}$  is elongational rate.  $\eta_e = 3\eta_0(1 + E_R)$ . When  $\dot{\epsilon} \rightarrow 0$ ,  $\eta_e = 3\eta_0$ . Figure 7 shows the strain hardening phenomena. Similar oscillatory behavior as seen in simple shear flow can be seen at a relatively higher elongational rate ( $\dot{\epsilon} = 10 \text{ s}^{-1}$ ). A comparison of the effects of strain rate between the simple shear flow and the simple elongational flow on the polymer chain structure is shown in Fig. 8. The change of both  $C_{11}$  and  $\det C$  are much bigger in the elongational flow than

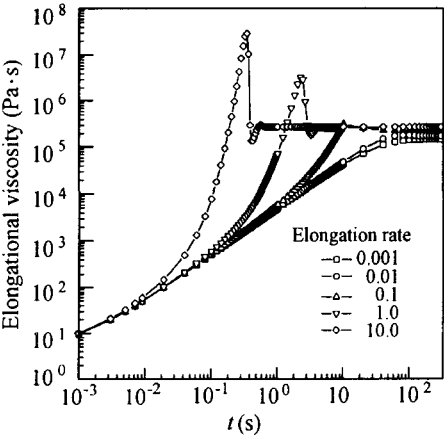


**Fig. 7** A plot of elongation viscosity versus time at different elongation rates

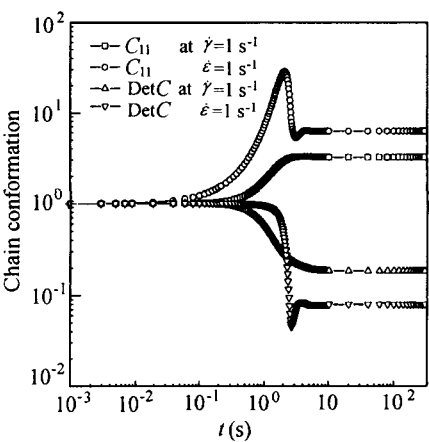


**Fig. 8** A comparison between shear and elongational flow

that in the shear flow, though  $\varepsilon$  equals to  $\dot{\gamma}$ . This fact means that elongational flow has a higher tendency to stretch and to align polymer chains. In other words, steady simple extension is “strong flow”, while steady simple shear is “weak flow” for polymer melts.

**Oscillatory Shear Flow**

$$\text{tg}\delta = 1/S_R = B, \quad G' = GS_R\text{cos}\delta/(1+S_R^2), \quad G'' = GS_R\text{sin}\delta/(1+S_R^2) \tag{10}$$

Where  $G'$  is storage modulus,  $G''$  - loss modulus and  $\text{tg}\delta$  is loss tangent. The change of storage and loss modulus with angular frequency  $\omega$  is expressed in Fig. 9.

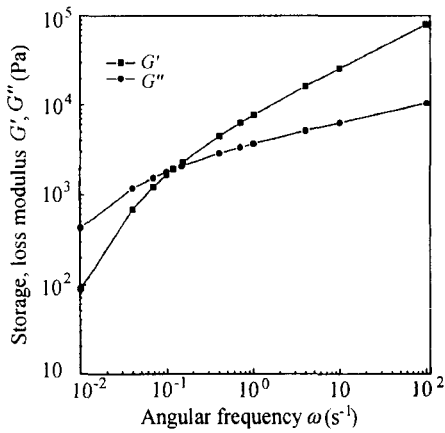


**Fig. 9** A plot of storage, loss modulus  $G'$ ,  $G''$  versus angular frequency  $\omega$

If we imposed an oscillatory shear on a steady simple shear flow field, the shear rate can be expressed as

$$\dot{\gamma} = \dot{\gamma}_o + \dot{\gamma}_a \cos(\omega t) \tag{10}$$

where  $\dot{\gamma}_o$  is the amplitude of shear rate in the steady simple shear flow,  $\dot{\gamma}_a = \omega\gamma_a$ ,  $\omega = 2\pi f$ ,  $\gamma_a$  is the oscillatory strain amplitude,  $f$  is the oscillatory frequency. The effects of the frequency  $f$  on shear stress  $\sigma_{12}$  as well as first normal stress difference  $N_1$  and second normal stress difference  $N_2$  are predicted in Fig. 10 where  $\dot{\gamma}_o = 10 \text{ s}^{-1}$  and  $\gamma_a = 0.1$ .  $N_2$  increases much faster than  $\sigma_{12}$  and  $N_1$  when  $f$  increases. Figure 11 shows the influence of amplitude  $\gamma_a$  on the second normal stress

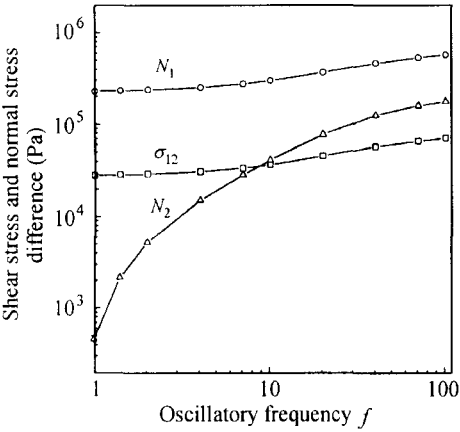


**Fig. 10** A plot of shear stress and normal stress difference versus oscillatory frequency

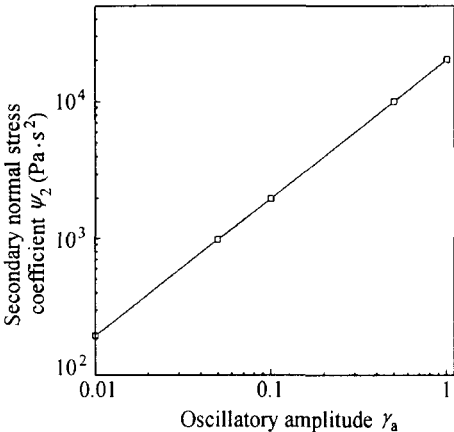


**Fig. 11** A plot of secondary normal stress coefficient  $\psi_2$  versus strain amplitude  $\gamma_a$

coefficient  $\psi_2$  at  $\dot{\gamma}_0 = 10 \text{ s}^{-1}$ . The result predicts that  $\psi_2$  increases with  $\gamma_a$ , which indicates that oscillatory shear imposed on a steady simple shear flow will benefit secondary flow as well as mixing effects as a consequence.

### Stress Relaxation after Flow Suddenly Stopped

$$C_{12} = C_{12}^0 \exp(-t/\lambda_1)$$

$$C_{11} - C_{22} = (C_{11} - C_{22})^0 \exp(-t/\lambda_1) \quad (11)$$

$$\sigma_{12} = G_S \exp(-t/\lambda_1) \quad (12)$$

$$N_1 = 2S_R^0 G_S \exp(-t/\lambda_1) \quad (13)$$

$$N_1 / \sigma_{12} = 2S_R^0 \quad (14)$$

Where  $G_S = G[S_R/(1+S_R^2)]^0$ , the superscript 'o' represents the moment the flow suddenly stopped. The relaxation processes of the shear modulus  $G$ , first normal stress difference  $N_1$ , and shear stress  $\sigma_{12}$  are expressed in Fig. 12.

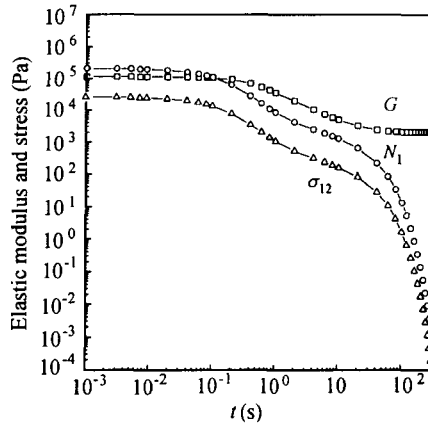


Fig. 12 A plot of modulus  $G$ , first normal stress difference  $N_1$ , and shear stress  $\sigma_{12}$  versus time

### CONCLUSIONS

Conceptually, the author assumes that there is an imagined conformation sphere to represent the shape of a polymer chain at rest, which is deformable and changed into a conformation ellipsoid in flow fields. The conformation sphere or ellipsoid is supposed to be equivalent to the volume element in the mathematical sense in continuum mechanics. Then a power law dependence of shear modulus of polymer melts on  $\det C$ , referred to as envelope volume, is proposed. Based on these assumptions, a rheological model of the internal structure of polymer melts into flow fields is derived according to Beris and Edwards' approach. The non-linear properties are introduced into the model by the power law dependence of shear modulus. The parameter  $n$  for this non-linear relation is just equal to the flow index of the power-law for non-Newtonian fluids. This is an advantage of the model for its application in polymer processing. The computation of the model has given a set of reasonable results, which describe the change of the internal structure and viscoelastic performance of polymer melts in different flow fields, such as simple shear flow, simple elongational flow, oscillatory shear flow, as well as the relaxation process after the flow suddenly stopped. A comparison between the predictions of the model and the experimental data for the viscoelasticity of LDPE in shear flow at 423 K shows that this model works well. Furthermore, the computation of  $\det C$  with time provides a possibility to describe the change of entanglement degree of polymer chains in flow fields. The model also predicted that an oscillation

of polymer chain occurs and behaves like an elastic material at the inception of steady shear flow or elongational flow, if the field force is very high and the polymer chain is not broken at that time. Another interesting prediction is that an oscillatory shear imposed on a steady simple shear flow causes an increase of the second normal stress coefficient, which will benefit secondary flow as well as mixing effects as a consequence.

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