

A Constitutive Model Describing Molecular Configuration Evolution and Transient Rheological Behavior of Entangled Polymer Solutions

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Abstract Entanglement network is an important structural feature in concentrated polymer solutions and polymer melts, which has a great influence on the transient rheological behavior and molecular configuration evolution. However, the existing constitutive models have limitations in describing the influence of dynamic entanglement behavior on molecular chain motion, resulting in inaccurate descriptions of the transient rheological behavior. Thus, a molecular configuration evolution model for polymer solutions considering the dynamic entanglement effect is proposed by introducing an intermolecular force that changes with the orientation of the molecular chain in this work. The intermolecular force is introduced by considering the friction coefficient as anisotropic, and the orientation effect is considered by introducing an excluded volume dependent anisotropic diffusion. The proposed model can better describe the stress relaxation, stress growth, and dielectric anisotropy of polymer solutions compared with the anisotropy FENE model and FENE model. In addition, the influence of different model parameters on the transient and steady shear response of polymer solution is investigated, and the results show that the influence of volume loss on the friction anisotropy factor k_G increases as the solution concentration increases.

Keywords Molecular configuration; Polymer solutions; Transient rheology; Dumbbell model

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INTRODUCTION

The flow of polymer solutions is everywhere, and almost all flows are accompanied by the dynamic evolution of molecular chain configuration.^[1] The entanglement network is an important structural feature in concentrated polymer solutions and melts, which has a great influence on transient rheological behavior and molecular configuration evolution. Research on the evolution behavior of molecular chains in entangled polymer solutions has been a challenging and hot subject for many years.^[2] However, the physical process of polymer molecular chain entanglement behavior is not fully understood.^[3] This is because the entangled molecular chain is intertwined with its neighboring molecular chains, resulting in a complex dynamic evolution of molecular chains in polymer solutions. The dynamic evolution of the microscopic configuration will affect the macroscopic flow of the polymer solution, thereby affecting the physical properties such as rheological, mechanical, optical, and dielectric properties of the polymer solution.^[4,5] Accurate prediction of the molecular configuration evolution behavior of polymer solutions is of significant importance for the performance customization of

the polymer product, for example, the favorable molecular orientation in polymer solar cells can greatly increase the efficiency of charge transfer, thereby increasing the efficiency of battery replacement.^[6,7] Therefore, it is very important to establish a polymeric configuration evolution model considering the influence of the dynamic orientation process on the intermolecular force.

The current configuration evolution models of polymer chains are basically for the unentangled molecular chain because the research on the evolution of molecular chains is still limited to a single molecular chain in polymer solutions due to the limitations of experimental methods.^[8,9] Spring-dumbbell based models such as the finitely extensible nonlinear elastic (FENE) model is the most commonly used molecular configuration evolution model for single molecular chain evolution in polymer solutions.^[10,11] For example, Griebel *et al.*^[12] simulated a 3D square-square contraction flow for polymer solution using the FENE model. Chauvière *et al.*^[13] simulated the flow process of dilute polymer solutions in planar homogeneous flows and the flow around a cylinder in a channel based on two-dimensional FENE dumbbells. Herrchen *et al.*^[14] used the FENE model to study the rheological behavior of polymer solutions in the steady-state and transient shear and extensional flow. Mu *et al.*^[15] simulated the three-dimensional flow process of viscoelastic fluid in a plane contraction flow using the Phan-Thien-Tanner (PTT), Giesekus and FENE

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models respectively and compared the simulated flow velocity, stress and birefringence results with the experimental results. However, the FENE model is not suitable for concentrated polymer solutions with entangled structure, because it does not consider the entanglement of the molecular chain and ignore the influence of surrounding molecular chains on the molecular configuration. There has also been some progress in molecular evolution models for concentrated polymer solution considering intermolecular force, for example, Schneggenburger *et al.*^[16] established an extended FENE dumbbell model by introducing the mean-field potential to consider the effect of anisotropy caused by intermolecular as well as intramolecular interactions in the polymer solution. Marrucci *et al.*^[17] realized the prediction of stress in steady-state and transient shear flow for polymer concentrated solution by introducing anisotropic diffusion coefficient into the classic dumbbell model. Kim *et al.*^[18] established an evolution model for molecular chains in unentangled polymeric liquids and semi-dilute solutions by introducing an anisotropic diffusion tensor. Song *et al.*^[19] considered the frictional force and Brownian force as anisotropy to reflect the influence of the wall on the restricted flow in a channel flow and studied the molecular tumbling of polymer chains near the wall. Sefiddashti *et al.*^[20] mentioned that the entanglement network of the molecular chains is almost destroyed at high shear rates, and molecular tumbling becomes the dominant dynamic response. Therefore, the forces between the molecular chains degenerate into single molecular chains at high shear rates. However, the models mentioned above did not consider the change of the intermolecular force with the dynamic orientation, resulting in the inaccurate prediction of the transient configuration evolution and material properties. Although the above model can obtain the steady results of the molecular configuration and rheological properties consistent with the experimental results by using appropriate model parameters, the influence of the transient orientation process on entanglement cannot be revised by constant model parameters. Therefore, the existing models cannot accurately describe the complex transient evolution behavior of entangled polymer molecular chains.

There are also researches that consider the loss of entanglement from flow in entangled polymers based on the PTT model. For example, Ferrás *et al.*^[21] proposed a modified Phan-Thien-Tanner (PTT) model to consider the destruction of physical network junctions and entanglements by introducing two extra constitutive parameters. However, the PTT model is proposed using the phenomenological method, which cannot describe microscopic behaviors related to molecular chains, such as the forces acting on molecular chains and the entanglement behavior between molecular chains. The model established by the molecular theory can intuitively describe the forces acting on molecular chains such as friction, Brownian force, *etc.*, thereby helping us to understand the entanglement behavior of polymer molecular chains more deeply. It is convenient and physical to consider the influence of entanglement behavior on the mechanical response through the change of the friction force acting on the molecular chain based on the molecular theory method.

The difficulty in establishing the molecular configuration

evolution model of entangled polymer solution is that the anisotropic forces between the molecular chains caused by the complex thermally-driven tangling (relaxation) and flow-driven untangling (orientation) behavior in the solution are very complicated. The tube model is the only molecular model that directly considers the entanglement of the molecular chain by restricting the movement of the molecular chain in a tube,^[3] and has made some progress in predicting the flow behavior of entangled polymer solutions.^[22–27] However, Sefiddashti *et al.*^[28] pointed out that the tube model has limitations in describing dynamic molecular chain behavior caused by the decrease in the number of entanglements and the increase in flow intensity. Therefore, the existing models fail to describe the transient rheology and configuration evolution of polymer solutions accurately. At the beginning of the polymer movement, the excluded volume of the molecular chains is the greatest, and the force between the molecular chains is the strongest. When the polymer solution concentration is extremely low or the molecular chains are completely untangled during the flow process, the force between the molecular chains gradually disappears. Therefore, a molecular configuration evolution model for polymer solutions considering the intermolecular force and volume change caused by dynamic orientation is established in this study. The intermolecular force is introduced by considering the friction coefficient as anisotropic, and the dynamic volume effect is considered by introducing a volume-dependent anisotropic diffusion. The proposed model is proven to better describe the transient rheological behavior and configuration evolution of polymer solutions.

The outline of this study is as follows: in **Section "Mathematical Model"** a molecular configuration evolution model for entangled polymer solutions considering the intermolecular force and dynamic orientation effect is proposed based on the dumbbell model, and the mathematical models between molecular configuration and material properties such as rheological properties, dielectric anisotropy, and birefringence are established. In **Section "Model Comparison and Verification"**, the proposed model is compared with the anisotropy FENE and FENE models to verify the accuracy of the proposed model in describing the rheological behavior and configuration evolution of molecular chains through the stress growth, stress relaxation, and dielectric anisotropy experiments of polymer solutions. Then the influence of different model parameters on the rheological behavior, configuration evolution, and performance of polymer solutions are studied in **Section "Influence of Model Parameters"**. Finally, we summarize the conclusion of this work.

MATHEMATICAL MODEL

Anisotropy FENE Model Considering Dynamic Effect

The FENE model based on the spring-dumbbell model is a commonly used model to describe the evolution of molecular chains in polymer solutions.^[3] However, the original FENE model is only applicable to the evolution of single molecular chains, and there are limitations in describing the evolution of molecular chains in entangled concentrated solutions. Kim *et al.*^[18] established the evolution model of the molecular chain of concentrated polymer solution by introducing an anisotropic

friction coefficient. However, the model does not consider the influence of the molecular chain dynamic orientation process (which leads to a change in the volume of the molecular chain) on the intermolecular force, thus failing to describe the transient behavior of the molecular chain accurately. To solve this problem, we introduce an excluded volume dependent anisotropic diffusion coefficient based on the anisotropic FENE model (AFENE model)^[18] to establish the anisotropic FENE model considering dynamic effect (AFENE-CE model), as shown in Fig. 1.

The molecular chains in the polymer dilute solution are affected by the four forces of friction, spring force, inertial force, and Brown force, respectively. The friction force on the molecular chain is caused by the speed difference between the polymer molecular chain and the solvent. According to Stokes' law, the friction force is expressed as:

$$F_f = -\zeta(\dot{\mathbf{r}}_i - \mathbf{u}(\mathbf{r}_i)) \quad (1)$$

where $\mathbf{u}(\mathbf{r}_i) = \mathbf{v}_0 + (\nabla \mathbf{v})^T \cdot \mathbf{r}_i$, $\mathbf{r}_i$ is the solvent speed, and ζ is friction coefficient, whose anisotropic form is expressed as:

$$\zeta = \zeta_0(\mathbf{u}\mathbf{u}^T + \sigma^{-1}(\mathbf{s}\mathbf{s}^T + \mathbf{t}\mathbf{t}^T)) \quad (2)$$

where ζ is the anisotropic friction coefficient tensor, $\mathbf{u}$ is a unit vector along the molecular chain bone (spring vector) direction, $\mathbf{s}$, $\mathbf{t}$ are the unit vectors orthogonal to $\mathbf{u}$ vector, and $\mathbf{s}\mathbf{s}^T + \mathbf{t}\mathbf{t}^T = \mathbf{I} - \mathbf{u}\mathbf{u}^T$, where $\mathbf{I}$ is the unit tensor. Therefore, the anisotropic friction coefficient can also be expressed as:

$$\zeta^{-1} = \frac{1}{\zeta_0}(\sigma \mathbf{I} + (1 - \sigma)\mathbf{u}\mathbf{u}^T) \quad (3)$$

where $\sigma = \kappa_1/\kappa_2$ is the friction coefficient anisotropy factor, κ_1 is the diffusion coefficient perpendicular to the molecular chain bone, and κ_2 is the diffusion coefficient along the molecular chain bone. Due to the influence of the nearby molecular chains, the molecular chains tend to move along the bone, that is $\kappa_1 < \kappa_2$ and $\sigma < 1$.

In the flow process of the polymer solution, the molecular chains experience both thermally-driven tangling and untangling caused by the shear flow. As a result, the excluded volume of the molecular chain and the force between molecules are constantly changing, causing the anisotropy factor

to change with the flow. The determinant of molecular configuration tensor ($\det \mathbf{C}$) is regarded as the relative volume contained in the flow field of a macromolecular chain. Under the action of the flow, the contained volume decreases continuously, indicating that other molecular chains are discharged and the untangling process continues. Zheng et al.^[29] found that $\det \mathbf{C}$ can be regarded as related to the excluded volume of the molecular chain in flow field: $V_{\text{ex}} = \det \mathbf{C}$, which is related to the degree of polymer chain entanglements. We approximate the influence of the dynamic entanglement behavior on the molecular chain orientation evolution by considering the change of the hydrodynamic anisotropy on the molecular chain with the excluded volume during the flow process. However, for different polymer solution systems, the excluded volume changes at a different speed, resulting in a different dependence on $\det \mathbf{C}$. Hence, we assume that the excluded volume for different polymer solutions can be expressed as:

$$V_{\text{ex}} = (\det \mathbf{C})^n \quad (4)$$

where $\mathbf{C}$ is the molecular configuration tensor, and n ($n > 0$) is a material parameter related to the speed of molecular chain volume changes. The larger the n , the faster the molecular chain volume changes with the orientation of the molecular chain. When $n=0$, the volume no longer changes with the flow.

In the initial configuration, the contained volume of the polymer molecular chain is the largest ($\det \mathbf{C}=1$) and the distance between molecular chains is the smallest, and the motion of the dumbbells is strongly affected by the nearby dumbbells. The movement of the molecular chain can be regarded as being restricted in a tube. That is, the free diffusibility in the direction of the molecular chain bone is much stronger than that in the direction perpendicular to the molecular chain bone, and the hydrodynamic anisotropy (entanglement) of the molecular chain is the strongest at this time. With the molecular chain orientation and untangling, $\det \mathbf{C}$ gradually decreases to 0. When the molecular chain is completely oriented (completely untangled), the effect of the surrounding molecular chain is almost negligible, and the free diffusibility anisotropy of the molecular chain disappears.

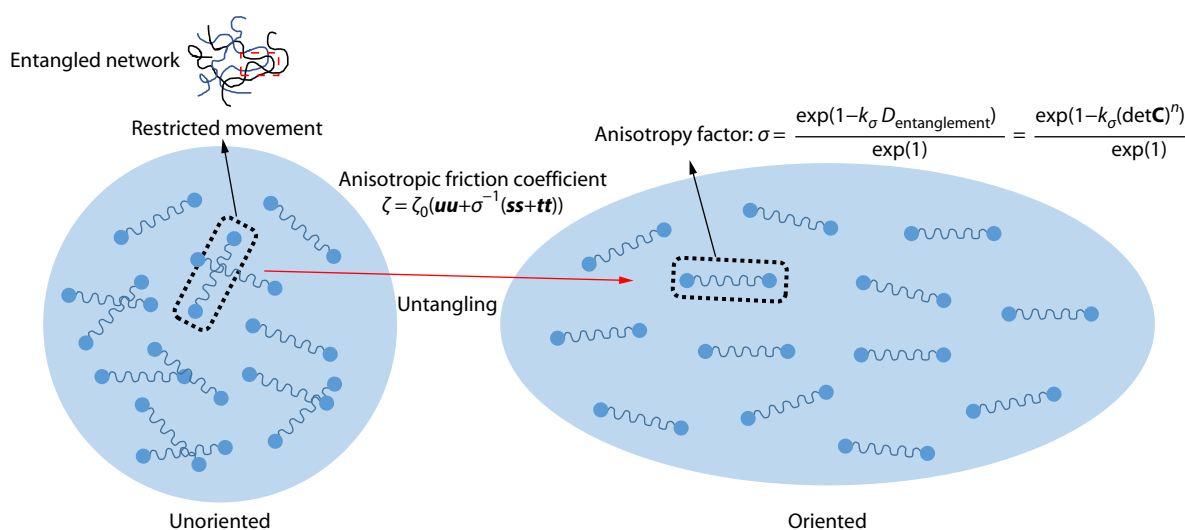


Fig. 1 The principle of the anisotropic FENE model considering dynamic effect.

Song *et al.*^[19] investigated the orientation and deformation of polymer chains in a confined microchannel. They assume that the friction coefficient is anisotropic and has a position dependence in the form of an exponential function. The tube model assumes that the motion of the tangled molecular chain is confined in the tube, which is somewhat similar to the movement of the molecular chain in a confined microchannel. Referring to Song's hypothesis, the following exponential form is used to describe the change of the anisotropy factor with the excluded volume.

$$\sigma = \frac{\exp(1 - k_\sigma(V_{\text{ex}}))}{\exp(1)} = \exp(-k_\sigma(\det \mathbf{C})^\eta) \quad (5)$$

where σ ($0 < \sigma < 1$) is the anisotropy factor, $\sigma_0 = \exp(-k_\sigma)$ is the initial anisotropy factor, and k_σ is a material parameter describing the influence of the volume loss on the friction anisotropy parameter.

When the model parameter $n=0$, the excluded volume no longer changes with the flow, and the AFENE-CE model degenerates to the AFENE model. When the model parameter $k_\sigma=0$, the AFENE-CE model degenerates to the FENE model. There is a containment relationship between AFENE-CE, AFENE, and FENE models, and their scope of application is AFENE-CE > AFENE > FENE. For dilute solutions or completely oriented molecular chains, the constraint of nearby molecular chains disappears, and the possibility of molecular chains moving in all directions is the same, that is $\sigma=1$, and anisotropic friction coefficient (Eq. 3) degenerates into isotropic.

Refer to the previous FENE^[19] model, the motion equations of two dumbbell balls can be expressed as:

$$m\ddot{\mathbf{r}}_i = -\zeta(\dot{\mathbf{r}}_i - \mathbf{v}(\mathbf{r}_i)) - kT\partial \ln \psi / \partial \mathbf{r}_i + H\mathbf{Q} / (1 - \mathbf{Q}^2 / Q_0^2) = 0 \quad (6)$$

Substitute in $\mathbf{Q} = \mathbf{r}_2 - \mathbf{r}_1$ to get:

$$\dot{\mathbf{Q}} = (\nabla \mathbf{v})^T \mathbf{Q} - 2kT\zeta^{-1} \partial \ln \psi / \partial \mathbf{Q} - 2\zeta^{-1} \mathbf{F}_e \quad (7)$$

The probability density distribution function of the dumbbell and the probability flux satisfy the following continuity equation.

$$\frac{\partial \psi}{\partial t} + \frac{\partial}{\partial \mathbf{Q}} \cdot (\dot{\mathbf{Q}} \psi) = 0 \quad (8)$$

Combining Eq. (7) and Eq. (8), the probability density distribution equation (Fokker-Plank equation) of dumbbell molecules is obtained:

$$\frac{\partial \psi}{\partial t} + [(\nabla \mathbf{v})^T \mathbf{Q}] \frac{\partial \psi}{\partial \mathbf{Q}} - 2kT\zeta^{-1} \frac{\partial^2 \psi}{\partial \mathbf{Q}^2} - 2\zeta^{-1} \frac{\partial (\psi \mathbf{F}_e)}{\partial \mathbf{Q}} = 0 \quad (9)$$

The ensemble average of the end vector distribution of dumbbell molecules is defined as:

$$\langle f(\mathbf{Q}) \rangle = \int f(\mathbf{Q}) \psi(\mathbf{Q}, t) d\mathbf{Q} \quad (10)$$

Then, the molecular configuration tensor $\langle \mathbf{Q}\mathbf{Q} \rangle$ and the dimensionless configuration tensor $\mathbf{C}$ can be defined as:

$$\langle \mathbf{Q}\mathbf{Q} \rangle = \int \mathbf{Q}\mathbf{Q} \psi(\mathbf{Q}, t) d\mathbf{Q} \quad (11)$$

$$\mathbf{C} = H \langle \mathbf{Q}\mathbf{Q} \rangle / kT \quad (12)$$

Combining the definition of molecular configuration tensor with the Fokker-Plank equation, the evolution equation of the molecular configuration tensor (AFENE-CE) can be obtained using Peterlin approximation.^[14]

$$\lambda \left(\frac{D\mathbf{C}}{Dt} - (\nabla \mathbf{v})^T \cdot \mathbf{C} - \mathbf{C} \cdot (\nabla \mathbf{v}) \right) = \exp(-k_\sigma(\det \mathbf{C})^\eta) \mathbf{I} - \frac{\mathbf{C}}{1 - \text{tr}(\mathbf{C})/b} + \frac{3\mathbf{C}}{\text{tr}(\mathbf{C})} (1 - \exp(-k_\sigma(\det \mathbf{C})^\eta)) \quad (13)$$

where $b = HQ_0^2/kT$ is the maximum stretch of the molecular chain after dimensionless, and $\lambda = \xi/4H$ is relaxation time.

When $n=0$ ($\sigma=\text{constant}$), the AFENE-CE model is equivalent to the AFENE model, and when the molecular chain is completely untangled ($\sigma=1$), the model degenerates into the spring dumbbell model for a single molecular chain (FENE model).

In simple shear flow, the evolution equation of the configuration tensor $\mathbf{C}$ can be simplified as:

$$\begin{aligned} \lambda \left(\frac{D\mathbf{C}_{xx}}{Dt} - 2\dot{\gamma}\mathbf{C}_{xy} \right) &= \sigma - \frac{\mathbf{C}_{xx}}{1 - \text{tr}(\mathbf{C})/b} + \frac{\mathbf{C}_{xx}}{\text{tr}(\mathbf{C})} (3 - 3\sigma) \\ \lambda \left(\frac{D\mathbf{C}_{xy}}{Dt} - \dot{\gamma}\mathbf{C}_{yy} \right) &= -\frac{\mathbf{C}_{xy}}{1 - \text{tr}(\mathbf{C})/b} + \frac{\mathbf{C}_{xy}}{\text{tr}(\mathbf{C})} (3 - 3\sigma) \\ \lambda \left(\frac{D\mathbf{C}_{yy}}{Dt} \right) &= \sigma - \frac{\mathbf{C}_{yy}}{1 - \text{tr}(\mathbf{C})/b} + \frac{\mathbf{C}_{yy}}{\text{tr}(\mathbf{C})} (3 - 3\sigma) \end{aligned} \quad (14)$$

Relationships between Molecular Configuration and Material Properties

In this part, the mathematical models between molecular configuration tensor and rheological properties, dielectric anisotropy, and birefringence are established to study the evolution behavior of polymer molecular chain configuration.

Molecular configuration

The configuration tensor is the probability average distribution of the polymer molecular chain within a certain range. The current configuration evolution models are all symmetric positive definite such as Maxwell, PTT, FENE, and Giesekus models,^[30] which means the existing polymer molecular configuration models assume that the average configuration of molecular chains is axisymmetric. An oriented ellipse is a commonly used description method to express the average configuration of polymer molecular chains.^[22,31] The symmetric positive definite configuration tensor can be represented by an orientation ellipsoid. The eigenvalue of the configuration tensor represents the length of the major axis of the configuration ellipsoid, and the eigenvector represents the direction of the major axis of the ellipsoid, as shown in Fig. 1. Therefore, the axisymmetric configuration ellipsoid is used to describe the average configuration of the molecular chain within a certain range in this study.

The configuration tensor can also be used to calculate related parameter information related to molecular chain orientation and deformation, for example, the orientation angle (θ) and the degree of stretching along the orientation direction (S) can be calculated as:

$$\theta = 1/2 \arctan(2\mathbf{C}_{xy} / (\mathbf{C}_{xx} - \mathbf{C}_{yy})) \quad (15)$$

$$S = \mathbf{C}_{11} / \text{Tr} \mathbf{C} \quad (16)$$

where $\mathbf{C}_{xx}$, $\mathbf{C}_{yy}$ and $\mathbf{C}_{xy}$ are the components of the configuration tensor $\mathbf{C}$, $\mathbf{C}_{11}$ is the main eigenvalues of $\mathbf{C}$, and $\text{Tr} \mathbf{C}$ is the trace of the configuration tensor $\mathbf{C}$.

Rheological properties

The orientation and disentanglement behaviors of the molecular chain under the action of the flow field will make the molecular chain easier to move along the direction of the flow, which is reflected in the macroscopically as an increase in shear stress and a decrease in viscosity. Therefore, a mathematical model between molecular configuration and shear stress, and viscosity is established in this section to verify the accuracy of the AFENE-CE model for predicting molecular configuration and rheological properties.

The stress tensor on the molecular chain is given by Kramers' expression:

$$\tau = G \left(\frac{\mathbf{C}}{1 - \text{Tr} \mathbf{C} / b} - \mathbf{I} \right) \quad (17)$$

Therefore, the shear stress and viscosity can be expressed as:

$$\tau_{xy} = G \left(\frac{C_{xy}}{1 - \text{Tr} \mathbf{C} / b} \right) \quad (18)$$

$$\eta = \tau_{xy} / \dot{\gamma} \quad (19)$$

where G is the shear modulus of the polymer solute.

Dielectric anisotropy

Since the evolution of the molecular chain configuration will lead to the change of molecular chain polarizability distribution, the orientation and deformation of the molecular chain configuration will cause the generation of dielectric anisotropy, that is, the dielectric response of the molecular chain in the electric field along and perpendicular to the flow direction is different. Therefore, the accuracy of the prediction of the molecular chain configuration evolution of the FENE-CE model can be verified by the dielectric anisotropy of the polymer solution.

Molecular polarizability is used as a bridge to establish the connection between molecular configuration and dielectric anisotropy. By combining the relationship between molecular polarizability and dielectric constant (generalized Clausius-Mossotti equation)^[32] and the relationship between molecular configuration and polarizability, the relationship between the molecular configuration tensor and the dielectric anisotropy is obtained. The details of the derivation process can be found in our recent work.^[33]

$$\begin{aligned} \epsilon_{r_{xx}} - \epsilon_{r_{yy}} &= \frac{1}{15} \frac{N_A}{M} (a_1 - a_2) \frac{(\epsilon_r + 2)^2}{\epsilon_0} (\mathbf{C}_{xx} - \mathbf{C}_{yy}) / \text{Tr}(\mathbf{C}) \\ &= K_\epsilon (\mathbf{C}_{xx} - \mathbf{C}_{yy}) / \text{Tr}(\mathbf{C}) \end{aligned} \quad (20)$$

where K_ϵ is a dimensionless quantity related to material properties, ϵ_r is the relative permittivity of material, and $\epsilon_{r_{xx}} - \epsilon_{r_{yy}}$ is the dielectric difference between the flow and the vertical flow direction, which represents dielectric anisotropy.

Birefringence

The orientation behavior of polymer molecular chains will cause changes in the refractive index of the molecular chains along the flow direction and perpendicular to the flow direction, resulting in birefringence. The mathematical model between molecular chain configuration and birefringence can be used to predict the evolution of optical properties during the forming process.

The relationship between birefringence and configuration tensor can be calculated by the configuration tensor. The de-

tails of the derivation process can be found in Ref. [33].

$$\Delta n_{xy} = K_n [(\mathbf{C}_{xx} - \mathbf{C}_{yy})^2 + 4\mathbf{C}_{xy}^2]^{1/2} / \text{Tr}(\mathbf{C}) \quad (21)$$

where K_n is a dimensionless quantity related to material properties, Δn_{xy} is the birefringence.

MODEL COMPARISON AND VERIFICATION

Transient Rheological Behavior

Stress relaxation and growth are the most typical transient rheological behavior in the polymer solution, which can reflect the dynamic orientation behavior in polymer solution macroscopically. The accuracy of the proposed AFENE-CE model to describe the stress relaxation and growth of polymer solutions in shear flow is investigated, in comparison with the AFENE model and FENE model.

Polystyrene (PS) is a linear long-chain polymer with an entangled structure, which is suitable for studying the influence of the untangling process. The molecular weight of PS is 2.07×10^5 Mw. The PS/DMF solutions were chosen to study the stress relaxation and growth process on a rotational rheometer (MCR 302, Anton Paar). The stress relaxation was obtained by observing the release process of the stress in the solution after applying step shear to the solution, and the stress growth was obtained by applying a constant shear rate to the solution. All experiments were performed at room temperature (30 °C).

Figs. 2(a) and 2(b) show the comparison of stress relaxation and dynamic shear viscosity for a 10 wt% PS/DMF solution after a step shear action with a shear rate of 1 s^{-1} and an action time of 5 s. The stress relaxation behavior macroscopically reflects the process of molecular chains retangling under the Brownian motion. Compared with the AFENE model and FENE model, the AFENE-CE model describes the stress relaxation and dynamic viscosity of polymer molecular chains more accurately. Fig. 2(c) shows the relative excluded volume changes with the flow process of polymer solution, and the excluded volume gradually increases from 0.2 to 1 in the relaxation process. It is because when the polymer solution stops flowing, the untangled and oriented molecular chains gradually retangling to the initial state. Fig. 2(d) shows anisotropy factors in the three models. The FENE model does not consider the influence of nearby molecular chains ($\sigma=1$), resulting in excessive stress release. The AFENE model does not consider the increase in diffusion anisotropy caused by the recovery of entanglement ($\sigma=\text{constant}$), which leads to slow stress release during the rapid recovery of the entanglement. The stress relaxation processes calculated by the AFENE model under different anisotropy factors are compared with the experimental results to investigate the effect of adjusting σ on the accuracy of the AFENE model prediction (as shown in Fig. 3). It is found that even if the value of the anisotropy factor σ is adjusted, the AFENE model cannot predict the stress relaxation process as accurately as the AFENE-CE model. It is because when the polymer solution stops flowing, the untangled and oriented molecular chains gradually retangling to the initial state, and the force between the surrounding molecular chains increases, increasing the anisotropy of the hydrodynamic. The constant anisotropy factor

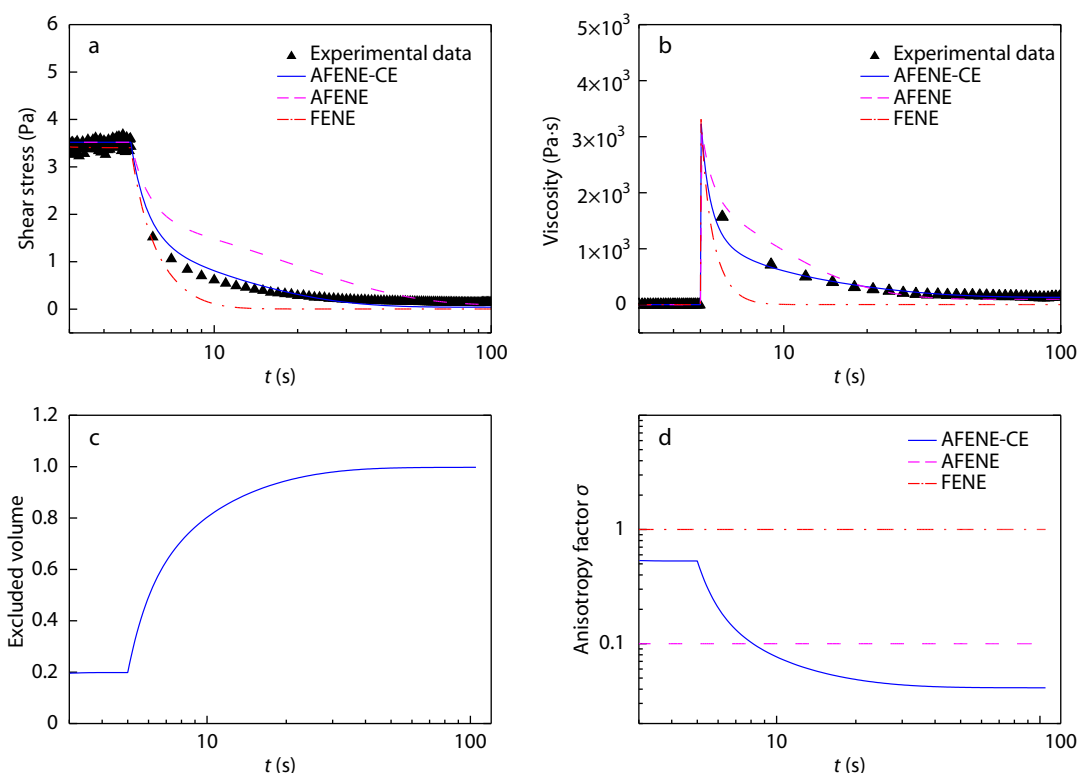


Fig. 2 Relaxation process of 10 wt% PS/DMF solution after shear flow stops: (a) shear stress growth, (b) dynamic viscosity growth, (c) relative excluded volume, and (d) anisotropy factor.

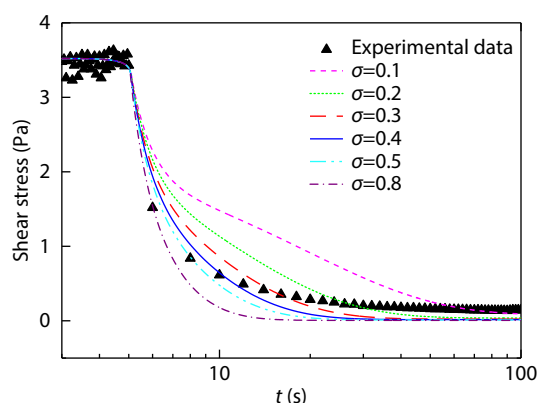


Fig. 3 Comparison between calculated stress relaxation by AFENE model under different anisotropy factor σ and measured results.

cannot describe the change of the hydrodynamic anisotropy with the molecular chain orientation, which leads to inaccurate predictions of transient rheological behavior.

Meanwhile, the comparison of the relaxation processes of PS/DMF solutions with different concentrations is presented in Fig. 4. The stress relaxation results of 5 wt% PS/DMF are obtained after a step shear action with a shear rate of 0.5 s^{-1} and an action time of 7 s. The stress relaxation results of 20 wt% PS/DMF are obtained after a step shear action with a shear rate of 1 s^{-1} and an action time of 5 s. It shows that the calculated results by the AFENE-CE model are highly consistent with the experimental results, while the AFENE model and FENE model fail to match the experiment, and the higher the

concentration, the greater the deviation from the experiments. Consequently, the AFENE model and FENE model fail to describe the dynamic rheological behavior of polymer solutions, especially for high concentration polymer solutions.

Therefore, the AFENE-CE model can better describe the transient rheological behavior of stress relaxation for polymer solutions with different concentrations.

Figs. 5(a) and 5(b) show the comparison between simulated results of the three models (AFENE-CE, AFENE, and FENE models) and the experimental results of stress growth and dynamic shear viscosity for a 10 wt% PS/DMF solution at a shear rate of 0.01 s^{-1} . The stress growth and dynamic viscosity change are caused by the orientation and untangling behavior of microscopic molecular chains. Figs. 5(a) and 5(b) clearly show the AFENE-CE model better describes the stress growth and dynamic viscosity of polymer molecular chains, which means the proposed model can better describe the orientation behavior of the molecular chain under the action of shear flow. Fig. 5(c) shows the relative excluded volume changes with the flow process of the polymer solution. When the polymer solution starts to flow, the molecular chains are gradually untangled and oriented along the flow direction under the action of the shear force (Fig. 5c), resulting in a change in the anisotropic diffusion of the molecular chain. When the molecular chain is completely oriented, the molecular chain diffusion coefficient degenerates to isotropic. Fig. 5(d) shows anisotropy factors in the AFENE-CE, AFENE, and FENE models. The closer the anisotropy factor is to 1, the weaker the anisotropy of molecular chain diffusion. The AFENE model and FENE model do not consider the change of anisotropy coefficient.

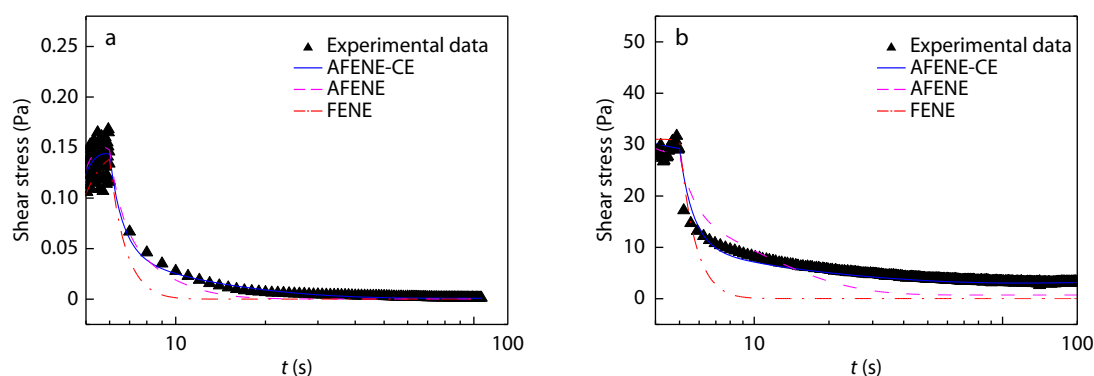


Fig. 4 Comparison of experimental and simulated results of the relaxation process of PS/DMF solutions with different concentrations: (a) 5 wt% PS/DMF and (b) 20 wt% PS/DMF.

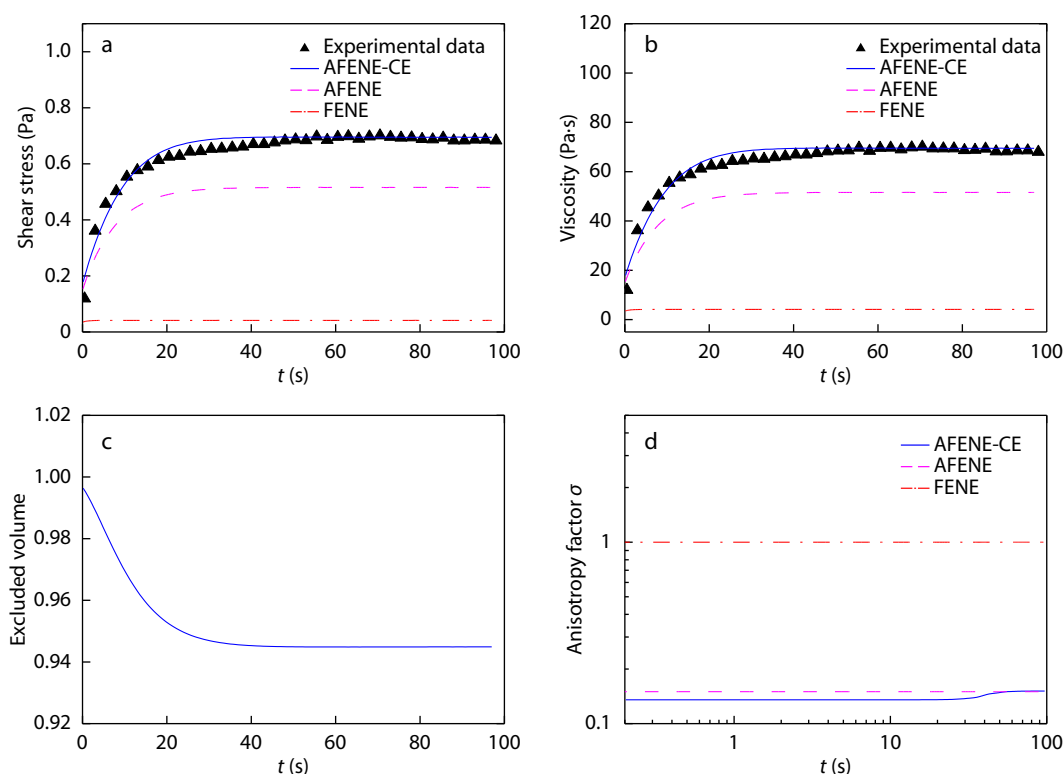


Fig. 5 Growth process of 10 wt% PS/DMF solution in shear flow: (a) shear stress growth, (b) dynamic viscosity growth, (c) relative excluded volume, and (d) anisotropy factor.

cient with the flow and treat the anisotropic diffusion factor as a constant. The present AFENE-CE model introduces a volume-dependent anisotropic diffusion coefficient to describe the influence of the orientation on the anisotropy of molecular chain diffusion. The subtle difference in the anisotropy coefficient of AFENE-CE model and AFENE model leads to significant differences in the development of stress on the macroscopic flow. Therefore, considering the influence of dynamic orientation behavior on the anisotropic diffusion coefficient of molecular chains is very important to accurately predict macroscopic flow behavior.

The simulation and experimental comparison of stress growth and relaxation under different start-up shear followed by flow cessation for the PS133k melt are shown in

Fig. 6(a). The comparison of extensional stress growth coefficient ($\eta_e = (\tau_{xx} - \tau_{yy})/\dot{\epsilon}$, $\dot{\epsilon}$ is the stretch rate) as a function of time at different stretch rates for PS285k/2k-47 is shown in **Fig. 6(b)**. The simulation results are calculated by the AFENE-CE model proposed in this study under the same group of parameters (as shown in **Table 1**), and the experimental results are taken from the literature.^[34] The predicted shear stress growth and relaxation under different shear rates and extensional stress coefficient η_e under different extensional rates are in good agreement with the experimental results, which proves that the proposed model can successfully predict the transient rheological behavior under different shear and extensional conditions with the same group of parameters.

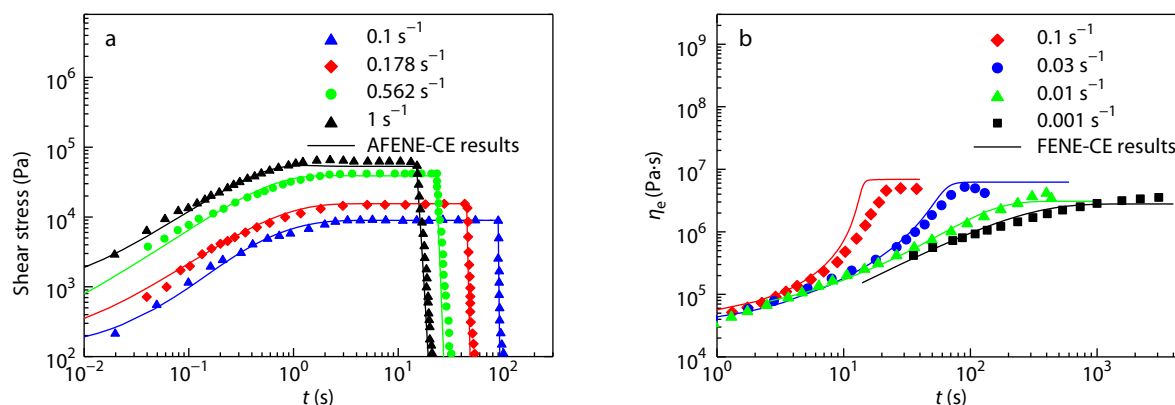


Fig. 6 Comparison between simulated (line) and experimental (symbols) results:^[33] (a) shear stress growth and relaxation for PS133k, (b) extensional stress growth coefficient for PS285k/2k-47.

Table 1 The parameters of the AFENE-CE model.

	c (mg/mL)	λ (s)	b	k_o	n	G
PS/DMF	5	1	10	1.2	1	0.15
PS/DMF	10	1.8	10	1.7	1	2.7
PS/DMF	20	2.3	10	3.0	1	18
PEO	1	0.025	1000	20	0.1	—
PS133k	—	0.3	5	1	1	98000
PS285k/2k-47	—	60	18	1.2	1	4000

Dielectric Anisotropy and Molecular Configuration Evolution

The dielectric anisotropy refers to the difference in the dielectric response of polymer molecular chains along and perpendicular

to the flow direction, which is related to the evolution of polymer molecular chain configuration. Our recent experimental and theoretical work has proven that the dielectric anisotropy of the polymer solution can be used to *in situ* characterize the molecular chain configuration evolution for different types of polymers.^[33,35] Thus, the accuracy of the AFENE-CE model in predicting the configuration evolution of the polymer molecular chain is verified by measuring the evolution of the dielectric anisotropy of the polymer solution.

The experimental principle and device details for measuring dielectric anisotropy can be found in Ref. [35]. The poly(ethylene oxide) (PEO) was selected as experimental material for its large molecular weight, long molecular chain, and

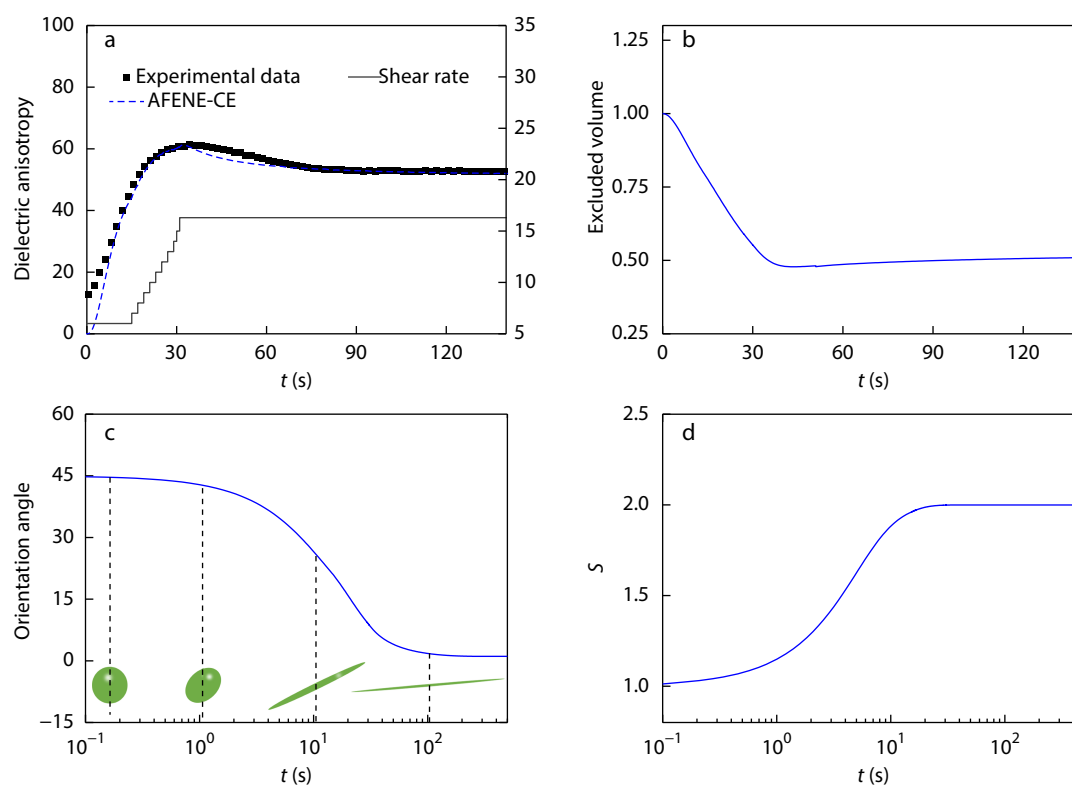


Fig. 7 Dynamic evolution of 1 wt% PEO aqueous solution in shear flow: (a) dielectric anisotropy, (b) relative excluded volume, (c) orientation angle, and (d) degree of deformation S .

complex entanglement structure. The molecular weight of the PEO is 5.0×10^6 Mw. The dielectric anisotropy coefficient of the 1 wt% PEO aqueous solution is $K_e = 11.2$.

Fig. 7 shows the dielectric anisotropy and molecular configuration evolution for a 1 wt% PEO aqueous solution in shear flow at a shear rate of 16.3 s^{-1} . The black solid line in Fig. 7(a) is the development curve of the shear rate over time. Since the rotor cannot immediately increase to the set speed, the shear rate has a gradual increase process. The blue solid line in Fig. 7(a) is the predicted dielectric anisotropy using the AFENE-CE model, and the black square symbols are the measured results. The predicted results of dielectric anisotropy are in good agreement with the measured results, indicating that the AFENE-CE model can accurately predict the dynamic evolution of molecular chain configuration (Fig. 7a). The evolution of the molecular chain excluded volume, orientation, and

deformation calculated by the AFENE-CE model are presented in Figs. 7(b)–7(d), and the evolution of the molecular chain configuration is presented in the bottom of Fig. 7(c). The orientation angle represents the degree of molecular chain orientation, and the degree of stretching along the orientation direction ($S = \mathbf{C}_{11}/\text{Tr}\mathbf{C}$) represents the degree of deformation. The closer the orientation angle is to 0, the greater the degree of orientation, and the larger the S , the greater the degree of deformation, when $S=2$, the molecular chain is fully stretched to Linear. The dielectric anisotropy increases first and then decreases to a certain equilibrium value, while the degree of the excluded volume decreases first and then increases to a certain equilibrium value (Figs. 7a and 7b). This means that the evolution of dielectric anisotropy is closely related to the configuration volume of molecular chains. The polymer chain experiences both thermally driven tangling

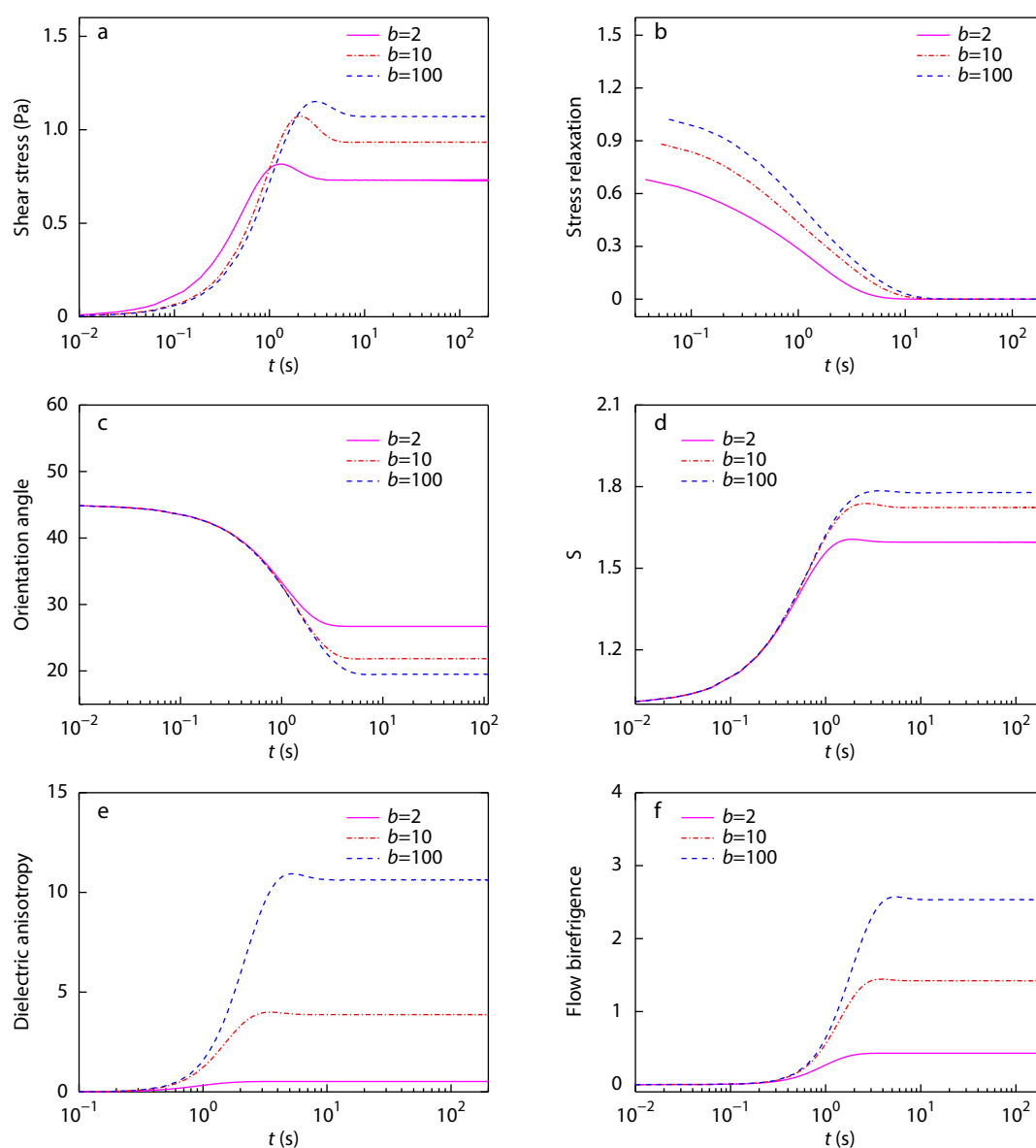


Fig. 8 The transient predicted results of the AFENE-CE model under different b ($k_a=1$, $\lambda=1$, $n=1$): (a) stress growth, (b) stress relaxation, (c) orientation angle, (d) degree of deformation S , (e) dielectric anisotropy, and (f) flow birefringence.

and untangling caused by shear flow. Initially, the molecular chains are in random spherical configuration and completely entangled, and the thermally driven tangling of the molecules is the weakest. Simultaneously, the untangling force (orientation) caused by shearing is much larger than thermally driven tangling, and thus the molecular chains rapidly disentangle along the flow direction. With the unentanglement of the molecular chains, the thermally driven tangling of the molecular chain gradually strengthened while the untangling caused by the shearing gradually weakened. When the untangling force caused by the shearing is reduced to less than the thermally driven tangling, the entanglement of the molecular chain begins to relax until the tangling force balances with the untangling force.

INFLUENCE OF MODEL PARAMETERS

There are four adjustable parameters in the molecular configuration evolution model proposed in this study, including the relaxation time λ and dimensionless constant b that represents the maximum extensibility of a dumbbell in the classic FENE model. Besides, this model adds two parameters k_G and n to describe the influence of molecular chain entanglement on anisotropic diffusion. The k_G is a material parameter describing the influence of the entanglement loss on the friction anisotropy parameter σ , and n is a material parameter related to the speed of molecular chain untangling.

The influence of the parameters b , k_G , λ and n on the evolution of molecular chain configuration and material properties

during the transient shear flow and steady shear flow are researched to determine the model parameters. Meanwhile, other material parameters remain constant, and $G=1$, $K_n=1$, $K_\epsilon=2$.

The Influence of b

The influence of parameter b on the transient flow process is studied. Fig. 8 shows the transient predicted results of the stress, configuration and material properties evolution of the AFENE-CE model under different b in a constant shear flow with a shear rate of 1 s^{-1} . The predicted stress growth and relaxation results of the molecular chain show that the stress at equilibrium increases as b increases, and the larger the b , the slower the stress growth and relaxation (Figs. 8a and 8b). Because b represents the length of the molecular chain, and the difficulty of disentanglement of molecular chains under shearing increases with the increase of the length of the molecular chain, that is, the resistance of the molecular chain movement increases as b increases. Therefore, the speed of growth and relaxation of the shear stress under shearing decrease with the increase of b , and the stress at equilibrium increases as b increases. The predicted molecular chain orientation angle and the degree of stretching along the orientation direction show that the degree of molecular chain orientation and stretching increase as b increases (Figs. 8c and 8d). Figs. 8(e) and 8(f) show that the predicted dielectric anisotropy and flow birefringence of the polymer solution show that material anisotropy properties also increase as b increases, which means material anisotropy properties are consistent with the change trend of

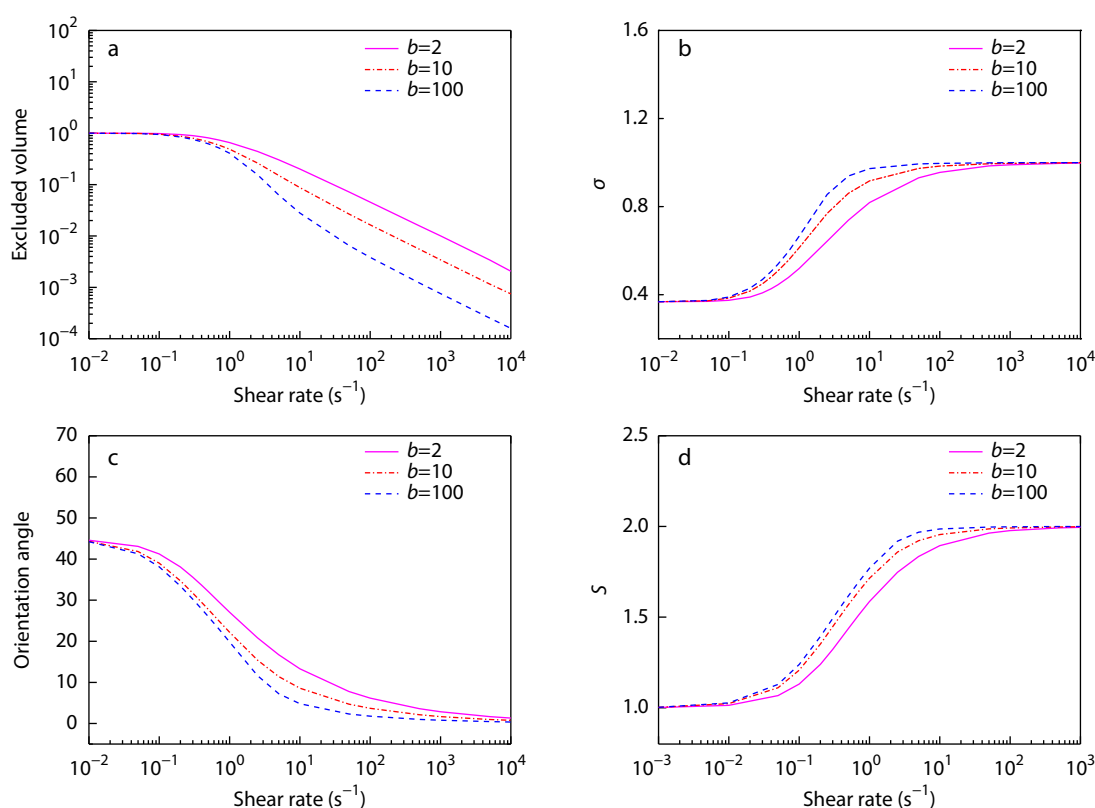


Fig. 9 The predicted results of the AFENE-CE model under different b in steady shear flow ($k_G=1$, $\lambda=1$, $n=1$): (a) relative excluded volume, (b) σ , (c) orientation angle, and (d) degree of deformation S .

molecular orientation and deformation.

Then, the influence of parameter b on the steady evolution is studied. Fig. 9 shows the predicted results of the relative excluded volume, anisotropy factor σ , orientation angle and the degree of stretching along the orientation direction S of the AFENE-CE model under different b in steady shear flow. Fig. 9(a) shows that the larger b is, the faster the excluded volume decreases with the increase of shear rate. Under the same shear rate, the longer the molecular chain, the smaller the excluded volume of the molecular chain, which causes the anisotropic diffusivity to decrease with the increase of b , that is, σ increases with the increase of b (Fig. 9b). The predicted molecular chain orientation angle and the degree of stretching along the orientation direction show that the larger b is, the faster the molecular chain orientation and stretching degree increase with the increase of shear

rate, which is consistent with the transient results (Figs. 9c and 9d).

The Influence of k_σ

Fig. 10 shows the transient predicted results of the stress, configuration and material properties evolution under different k_σ in a constant shear flow with a shear rate of 0.5 s^{-1} . The predicted stress growth of the molecular chain show that the stress overshoot and the stress at equilibrium increase as k_σ increases, and the larger the k_σ , the faster the stress growth (Fig. 10a). The predicted stress relaxation of the molecular chain show that the speed of the stress relaxation decreases as k_σ increases (Fig. 10b). The k_σ represents dependence degree of the anisotropy factor on the excluded volume. The larger the k_σ , the faster the diffusion anisotropy decreases during the orientation, and the faster the diffusion anisotropy rises during

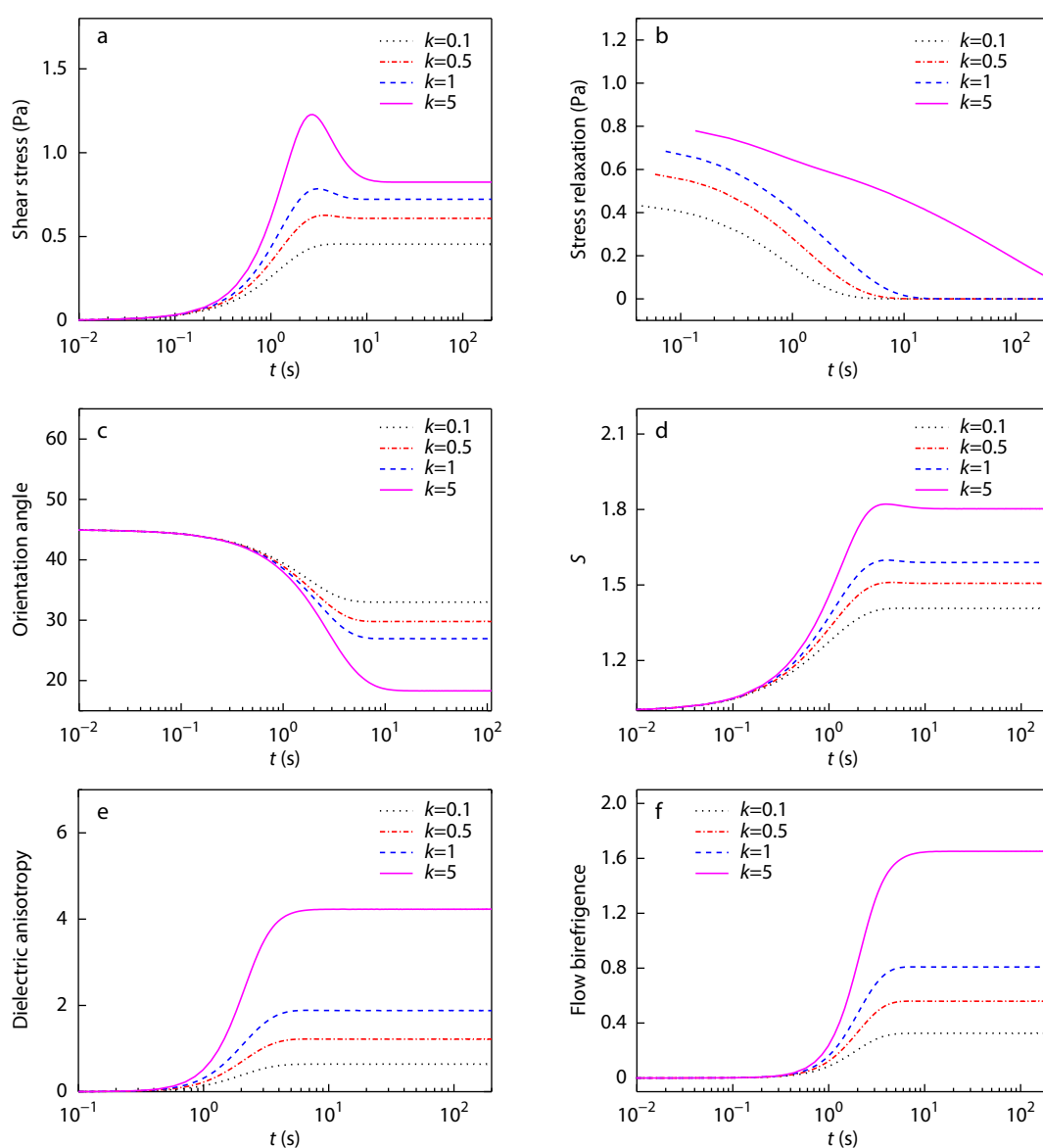


Fig. 10 The transient predicted results of the AFENE-CE model under different k_σ ($b=1$, $\lambda=1$, $n=1$): (a) stress growth, (b) stress relaxation, (c) orientation angle, (d) degree of deformation S , (e) dielectric anisotropy, and (f) flow birefringence.

the relaxation. Therefore, the larger the k_σ , the faster the stress growth and the slower the stress relaxation. The predicted molecular chain orientation angle and the degree of stretching along the orientation direction show that the degree of molecular chain orientation and stretching increase as k_σ increases (Figs. 10c and 10d). It is because the larger the k_σ , the stronger the anisotropy of the molecular chain, and so the easier it is to deform and orientation along the bone of the molecular chain. The predicted dielectric anisotropy and flow birefringence of the polymer solution show that material anisotropy properties increase as k_σ increases (Figs. 10e and 10f), which is consistent with the change trend of molecular orientation and deformation with k_σ .

The steady predicted results of the degree of entanglement and anisotropy factor σ under different k_σ are shown in Fig. 11. The parameter k_σ mainly affects the anisotropy factor σ , and has little effect on the excluded volume, because k_σ represents dependence degree of σ on the excluded volume, and has nothing to do with the excluded volume itself. In addition, the parameter k_σ mainly affects the molecular chain behavior at low shear rate, because the molecular chain has been completely untangled at high shear rate, and the anisotropy effect is almost negligible. At a constant shear rate, the larger the k_σ , the stronger the anisotropy of the molecular chain, and the stronger molecular chain orientation and deformation, which explains the previous transient behavior.

The Influence of λ

Fig. 12 shows the transient predicted results of the stress, configuration and material properties evolution under different λ in a constant shear flow with a shear rate of 1 s^{-1} . The predicted stress growth and relaxation of the molecular chain show that the stress overshoot and the stress at equilibrium increase as λ increases, and the speed of the stress growth and relaxation increase as λ increases (Figs. 12a and 12b). The parameter λ is the relaxation time of polymer chain, which represents the difficulty degree of molecular chains tangling. The longer the relaxation time, the more difficult the molecular chain to tangle and the easier to untangle. Therefore, the influence of nearby molecular chains increases with increasing relaxation time, resulting in the increase of stress growth and relaxation speed with the increase of relaxation time. The predicted molecular chain orientation angle and the degree of stretching along the orientation direction show that the degree of molecular chain orientation and stretching increase as λ increases, and the orientation and stretching speed also increase with the increase of λ (Figs. 12c and 12d). It is because the larger the λ , the larger the degree of molecular chain entanglement, the stronger the anisotropy of the molecular chain, and so the easier it is to deform the orientation along the bone of the molecular chain. The predicted dielectric anisotropy and flow birefringence of the polymer solution show that the overshoot and the equilibrium value of dielectric anisotropy and flow birefringence increase as λ increases, and the larger the λ , the faster the growth rate of dielectric anisotropy and flow birefringence (Figs. 12e and 12f).

The Influence of n

The transient predicted results under different n in a constant shear flow with a shear rate of 1 s^{-1} are shown in Fig. 13. It is

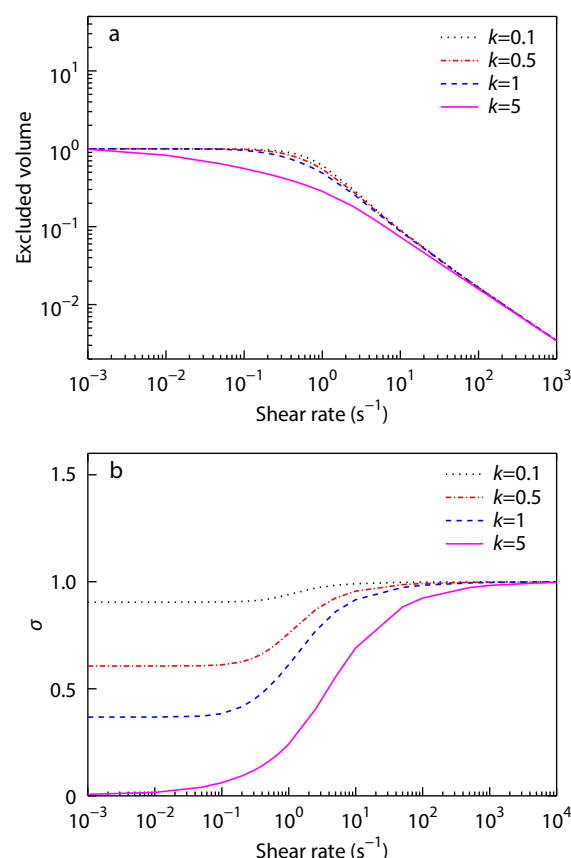


Fig. 11 The predicted results of the AFENE-CE model under different k_σ ($b=1$, $\lambda=1$, $n=1$) in steady shear flow: (a) degree of entanglement, and (b) anisotropy factor.

shown that the parameter n has almost no effect on the stress, orientation and material properties development of the transient process, and mainly affects the result of reaching the steady state. The predicted stress growth of the molecular chain show that the stress overshoot increase as n decreases (Fig. 13a). In addition, the degree of molecular chain orientation and deformation, as well as anisotropic properties such as dielectric anisotropy and flow birefringence, all increase as n decreases (Figs. 13c–13f). It is because the parameter n represents the speed of molecular chain volume changes with orientation, the smaller the n , the slower the excluded volume decreases with the molecular chain orientation process. Therefore, the degree of molecular orientation and deformation is greater for the same excluded volume.

Combining the experimental results and the above study on the law of model parameters, the model parameters of the solution system used in Section "Mathematical Model" are obtained, as shown in Table 1. It shows that the maximum molecular chain length b and molecular chain excluded volume factor n have nothing to do with the concentration of the solution, only related to the polymer type. For the same solution system, the relaxation time λ and the k_σ increase as the solution concentration increases. Because the higher the concentration of the solution, the stronger the elasticity of the molecular chain and the weaker the viscosity. For purely elastic objects, the relaxation time is infinitely large, while for

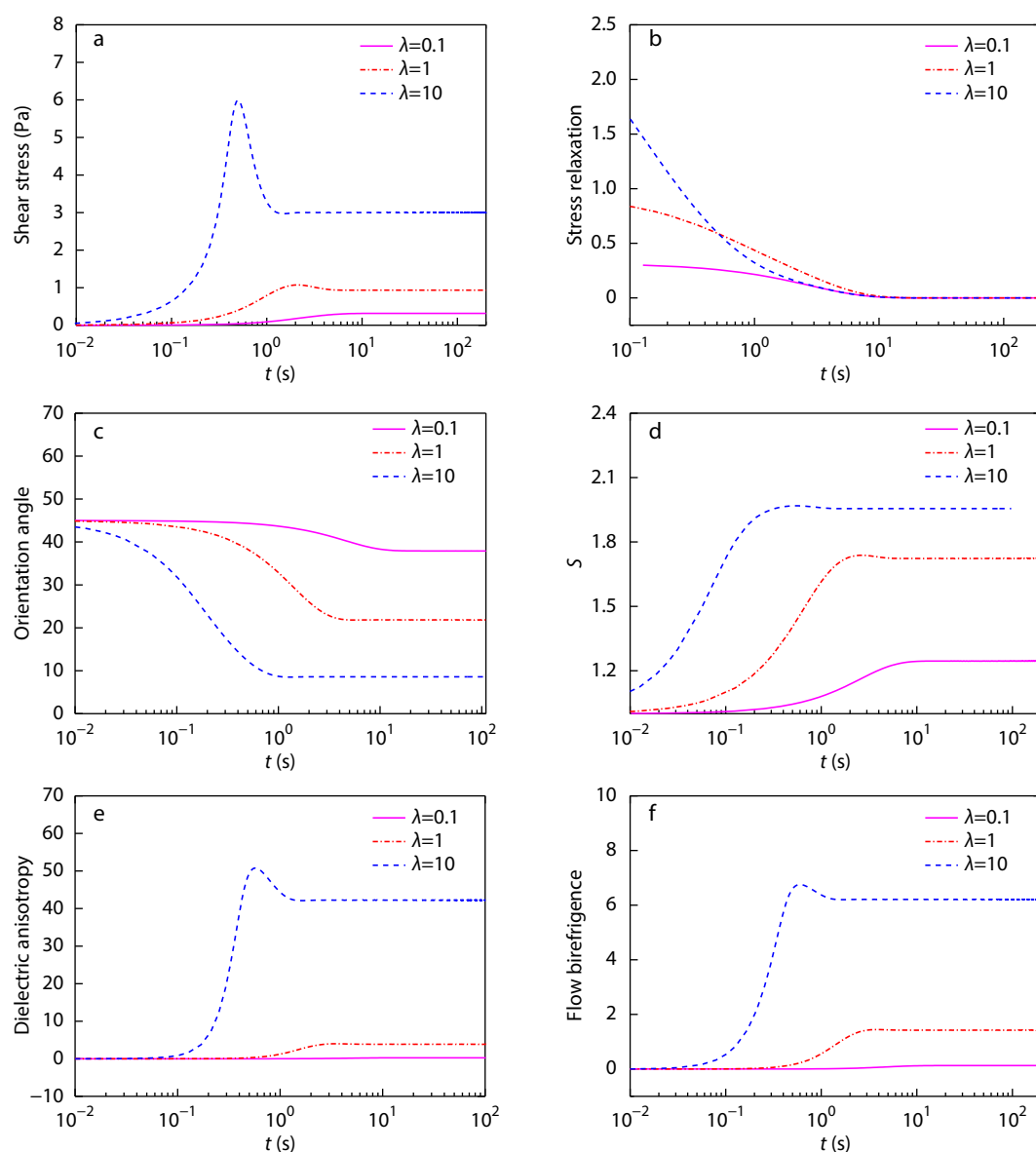


Fig. 12 The transient predicted results of the AFENE-CE model under different λ ($k_o=1$, $b=10$, $n=1$): (a) stress growth, (b) stress relaxation, (c) orientation angle, (d) degree of deformation S , (e) dielectric anisotropy, and (f) flow birefringence.

purely viscous objects, the relaxation time is infinitely small. In particular, very dilute polymer solutions are generally regarded as pure viscous Newtonian fluids. Therefore, the λ increases with increasing concentration, which is consistent with physical facts. In addition, the anisotropy of molecular chain diffusion increases as the concentration increases, resulting in greater k_o . The shear modulus G increases with increasing solution concentration, because the degree of entanglement between molecular chains increases as the concentration of the solution increases, resulting in the difficulty of the molecular chain movement. The molecular weight and molecular chain length of PEO are much larger than those of PS. Therefore, the parameter b of PEO is much larger than that of PS, and the relaxation time is much smaller than that of PS, even if the concentration of PEO solution is lower than that of PS solution. Meanwhile, the entanglement structure of PEO is

much more complex than that of PS, resulting in a slower untangling speed and larger diffusion anisotropy of molecular chains compared to PS. Therefore, the parameter n of PEO is smaller, and the k_o is bigger.

CONCLUSIONS

A model of molecular configuration evolution for polymer solutions considering the dynamic entanglement effect is established by introducing an anisotropic friction coefficient to consider the force of surrounding molecules, and introducing the idea of an excluded volume dependent anisotropic diffusion to consider the influence of molecular chain orientation on intermolecular forces. Transient rheological behavior and configuration evolution of polymer solutions are examined by experiments and simulations, compared with the Anisotropy

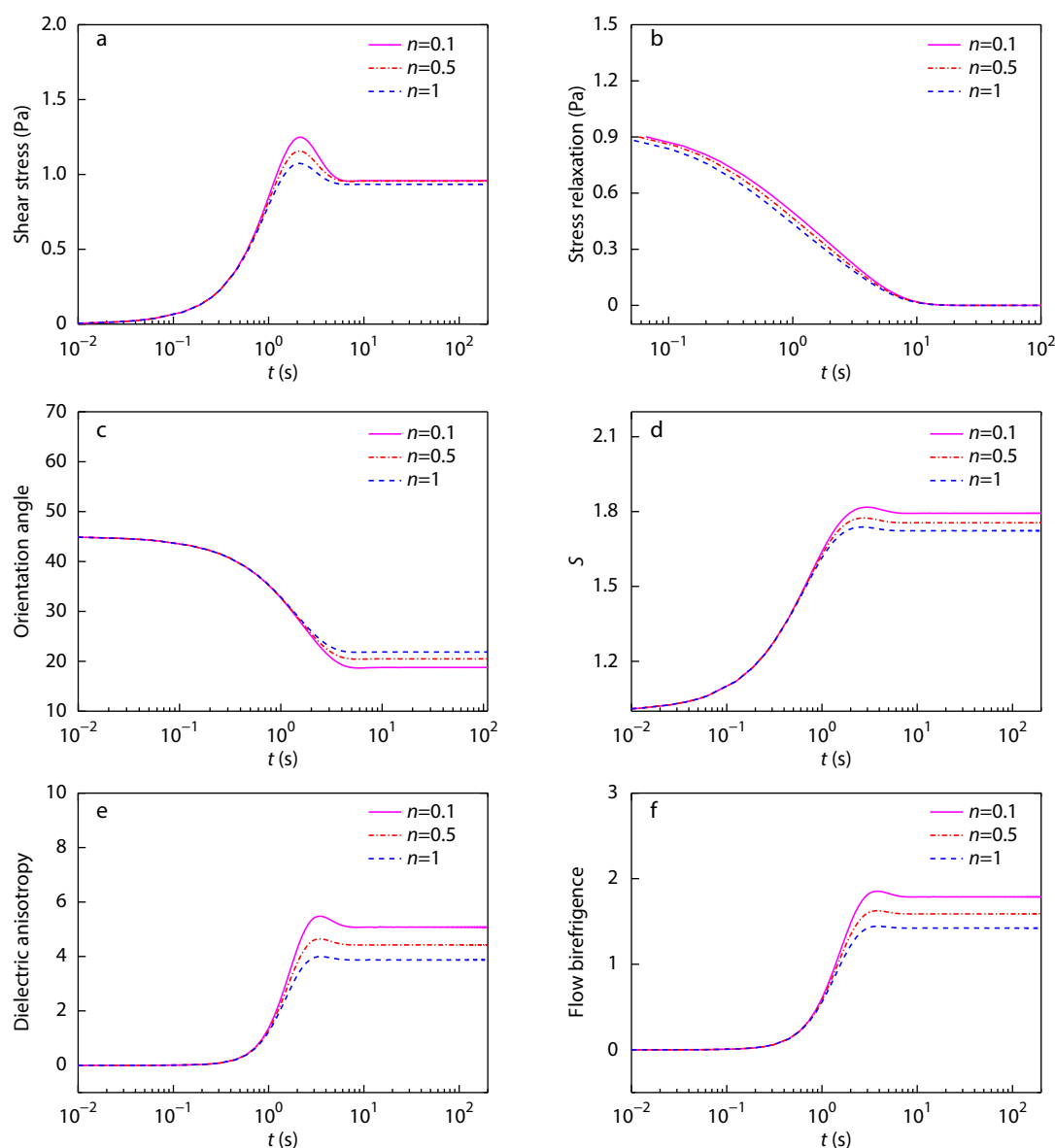


Fig. 13 The transient predicted results of the AFENE-CE model under different n ($k_{\sigma}=1$, $\lambda=1$, $b=10$): (a) stress growth, (b) stress relaxation, (c) orientation angle, (d) degree of deformation S , (e) dielectric anisotropy, and (f) flow birefringence.

FENE model and FENE model, and the proposed AFENE-CE model more accurately describes the stress growth and stress relaxation of polymer solutions, which means the modified model can better describe the transient rheological behavior of polymer solutions. Meanwhile, the AFENE-CE model more accurately describes the dielectric anisotropy of polymer solutions, which means that the modified model can better describe the configuration evolution of polymer solutions. Transient and steady-state shear response of polymer solution are studied *via* the AFENE-CE model under different model parameters. It is found that the parameters b and n are only related to the type of polymer, while the parameters λ and k_{σ} are not only related to the type of polymer, but also the concentration of the polymer solution, and the larger the solution concentration, the larger the relaxation time λ and k_{σ} .

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